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(DOKLADY AKADEMII NAUK SSSR)

Chemistry Section

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ON THE PRODUCTS OF THE REACTION OF OXIDES OF α-PINENE AND Δ^3-CARENE WITH ACETIC ANHYDRIDE

Academian B. A. Arbuzov and Z. G. Isaeva

In 1953, in a continuation of our work on the investigation of the isomeric transformations of bicyclic terpene hydrocarbons, we began a study of the reaction of α-pinene, Δ^3-carene, and camphene with acetic anhydride.

It was shown that the reaction of bicyclic terpene oxides with acetic anhydride proceeds in a complex manner with the formation of a mixture of products, and is accompanied by isomerization of the oxides.

The action of acetic anhydride on camphene oxide yields camphenilanaldehyde, the acetate of the enol form of camphenilanaldehyde, and the diacetate of 2,10-camphanediol. Three substances were also isolated from the products of the reaction of α-pinene with acetic anhydride: these were campholenaldehyde, the diacetate of sobrerol, and the acetate of an unsaturated alcohol having the composition $C_{12}H_{18}O_2$. A similar product was obtained from Δ^3-carene oxide (along with the diacetate of β-carene glycol). We did not investigate the structures of these compounds.

The present work had as its aim the determination of the structure of the acetates from α-pinene and Δ^3-carene.

There have recently appeared in the literature two reports by A. Kergomard on the study of the action of acetic anhydride on limonene oxide [1] and on the synthesis of perillyl alcohol [2], on the basis of which a reaction was proposed for the interaction of β-pinene oxide with acetic anhydride. Since this work is of a similar nature to our investigations on the isomeric transformations of bicyclic terpene oxides in their reactions with acetic anhydride, we are publishing the data which we have obtained up to the present on the study of the structure of the acetates mentioned above. As has been shown previously [3], the yield of the acetate $C_{12}H_{18}O_2$ does not exceed 30% for α-pinene and 22% in the case of Δ^3-carene oxide. According to the mechanism proposed by us for the reaction of oxides with acetic anhydride, it would be expected that the formation of $C_{12}H_{18}O_2$ acetates would become the predominant course of the reaction in the presence of the substance bound to an acetate ion, leading, consequently, to the formation of a minimum of acetates of diols. With the aim of confirming this assumption and of obtaining the acetate $C_{12}H_{18}O_2$ in high yield, the reaction of α-pinene with acetic anhydride was carried out in the presence of $NaHCO_3$. The experiment showed that 40% of the α-pinene was recovered unchanged: the isomerization of the oxide to campholenaldehyde proceeded to a considerably lesser extent. In place of the expected acetate, an alcohol having the composition $C_{10}H_{16}O$ was isolated from the reaction products in a yield of 28%; its constants were: b.p. 93.5-96°/6mm; $n^{20}D$ 1.4972, d^{20}_4 0.9544, MR_{found} 46.62, calculated for $C_{10}H_{16}OF_2$, 46.77, which is identical with DL-trans-carveol [4]. The acid phthalate ester had m.p. of 136-137°; literature data [5]: m.p. acid phthalate ester of DL-carveol, 136-136.5°. The 3,5-dinitrobenzoate had a rather wide m.p. range, 108-113° in spite of repeated recrystallization; the m.p. of the 3,5-dinitrobenzoate of DL-trans-carveol is 119°, while this value is 91.5° for DL-cis-carveol [4].

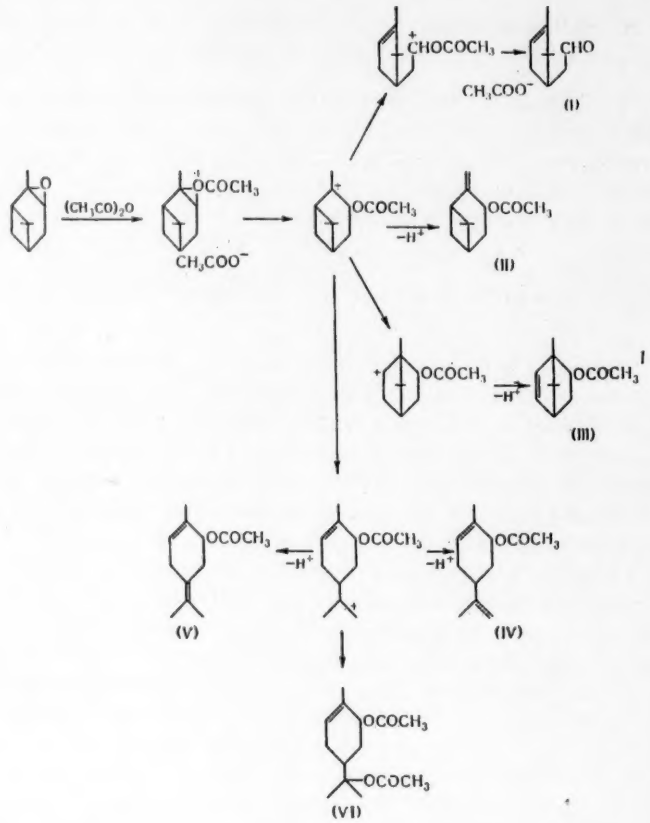
Carvone was obtained on oxidation of the alcohol with chromic anhydride in acetic acid: b.p. 94-97°/6.5 mm; $n^{20}D$ 1.4955; d^{20}_4 0.9663, MR_{found} 45.30; $C_{10}H_{14}O$ F_2 MR_{calc} 45.26; yield 47%. The carvone was identified by preparation of the hydrogen sulfide reaction product with a m.p. of 189-191° (m.p. H_2S reaction product of DL-carvone, 189-190° [5]).

From the data in reference [3], it is apparent that the boiling point of the acetate from α-pinene oxide lies within a wide temperature interval. With the goal of isolating the individual products, the reaction mixture from the reaction of α-pinene oxide and acetic anhydride was repeatedly fractionated in a column with an efficiency of 27 theoretical plates. Besides campholenaldehyde and the acetate of sobrerol, we obtained three substances having the same composition, $C_{12}H_{18}O_2$* (31% overall yield).

1. The low-boiling product 33.3% of the total weight of the $C_{12}H_{18}O_2$ products) had the constants: b.p. 79-80°/3 mm; $n^{20}D$ 1.4783, d^{20}_4 0.9921, $[\alpha]_D = +7°$ (2.85% in ethanol). MR_{found} 55.38; $C_{12}H_{18}O_2$ F_1, 4-membered ring, MR_{calc} 55.10. Titration with perphthalic acid revealed that a molecule of the product has 1 double bond.

Saponification with a 7% aqueous-alcoholic solution of NaOH gave a $C_{10}H_{16}O$ alcohol with the constants: b.p. 67.5-70°/2.5 mm; $n^{20}D$ 1.4992, d^{20}_4 0.9777, $[\alpha]_D = -50.1°$ (1.9% in ethanol) MR_{found} 45.66, $C_{10}H_{16}O$ F_1, 4-membered ring, MR_{calc} 45.50.

3,5-Dinitrobenzoate, m.p. 122-123.5°; phenylurethan, m.p. 96-97.5°; p-nitrobenzoate, m.p. 66.5-68°. According to our previously proposed "onium" mechanism for the reaction of α-oxides, the interaction of α-pinene oxide with acetic anhydride would be expected to form the following products:



* Experiments on the preparation of maleic anhydride addition products of the $C_{12}H_{18}O_2$ acetates from α-pinene oxide and from Δ^3 – carene oxide [3] were not reproducible.

Consequently, our bicyclic unsaturated alcohol with 1 double bond in the molecule could be identical with one of the pinocarveols (II). According to boiling point, $n^{20}D$, d^{20}_4 and $[\alpha]_D$, the alcohol more nearly resembled trans-pinocarveol [7]. However, the data on the crystalline derivatives were not in complete agreement with this: according to [7], the m.p. of the phenylurethan of transpinocarveol is 96-97°; and the m.p. of the p-nitrobenzoate is 93.5-94.5°. According to the data of Schmidt [8], the phenylurethan of trans-pinocarveol melts at 88-90°, and hydration of trans-pinocarveol with dilute sulfuric acid gives a hydrate with a m.p. of 190-191°, which we were unable to prepare. cis-Pinocarveol does not form a hydrate, but neither does it form many other derivatives; it does form a p-nitrobenzoate with a m.p. of 104° [9]. Our acetate of the bicyclic unsaturated alcohol could have the structure (III). We were unable to find any literature data on this acetate or on the corresponding alcohol.

2. The constants of the second $C_{12}H_{18}O_2$ product from the reaction of α-pinene oxide with acetic anhydride (the relative content in the mixture of $C_{12}H_{18}O_2$ products was 46.5%) were: b.p. 87-87.5°/3 mm; $n^{20}D$ 1.4747, d^{20}_4 0.9707, $[\alpha]_D$ = + 100.5° (1.86% in ethanol); MR_{found} 56.24, $C_{12}H_{18}O_2$ F_2 MR_{calc} 56.14 Titration with perphthalic acid indicated that the product contained 2 double bonds in the molecule.

Saponification of the acetate with aqueous-alcoholic NaOH (10%) gave an alcohol of the composition $C_{10}H_{16}O$ (yield 89.2%) with the constants: b.p. 86-87°/3 mm; $n^{20}D$ 1.4954, d^{20}_4 0.9510 $[\alpha]_D$ = + 115.6° (2.77% in ethanol); MR_{found} 46.65, $C_{10}H_{16}O$ F_2 MR_{calc} 46.77; 3,5-dinitrobenzoate, m.p. 120-121°; p-nitrobenzoate, m.p. 101.5-102.5°.

The reaction of α-pinene oxide with acetic anhydride would be expected to yield two acetates of monocyclic alcohols: the acetate of carveol (IV) and an acetate of the structure (V). A comparison with the literature data shows that the constants of the described alcohol are close to those of trans-carveol. However, the 3,5-dinitrobenzoate and the p-nitrobenzoate differed considerably in m.p. from the corresponding derivatives of trans-carveol.

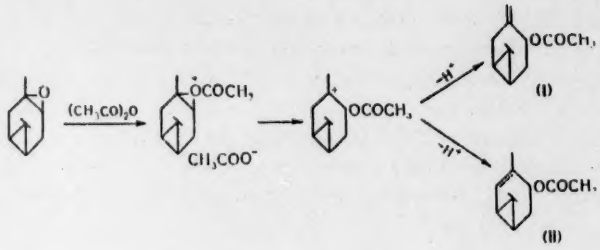
Oxidation of the alcohol with chromic anhydride in acetic acid gave a 49% yield of a ketone with the constants: b.p. 86.5-88°/6 mm; $n^{20}D$ 1.4949, d^{20}_4 0.9659, $[\alpha]_D$ = + 24.97° (3.78% in ethanol); MR_{found} 45.31; $C_{10}H_{14}O$ F_2 MR_{calc} 45.26. Phenylhydrazone, m.p. 108-108.5°; a mixed sample with the phenylhydrazone of D-carvone (m.p. 107-108°) melted without depression of the melting point (106.5-108°).

3. The third product of the composition $C_{12}H_{18}O_2$ (relative yield 20.1%) had the constants: b.p. 89-89.5°/3 mm; $n^{20}D$ 1.4844, d^{20}_4 0.9809, $[\alpha]_D$ = + 23.50° (1.75% in ethanol) MR_{found} 56.61, $C_{12}H_{18}O_2$ F_2 MR_{calc} 56.14. The investigation of this product is in progress.

An investigation of the composition of the products of the interaction of Δ^3-carene oxide with acetic anhydride showed that the reaction does not proceed smoothly. The composition of the reaction products (yields indicated on the basis of the oxide taken) was: 1) hydrocarbon fractions with $n^{20}D$ 1.4875-1.4913, d^{20}_4 0.8615-0.8787 3.5%; 2) carbonyl-containing products 7%; 3) $C_{12}H_{18}O_2$ acetate 14%; 4) the diacetate of β-carene glycol 13%.

Two carbonyl compounds were apparently formed in the reaction: 2 semicarbazones were obtained with melting points of 205-207 and 222-224° (with decomposition). The $C_{12}H_{18}O_2$ acetate(cf. above) had the constants: b.p. 86.5°/3.5 mm; $n^{20}D$ 1.4746, d^{20}_4 0.9864, $[\alpha]_D$ = − 44.01° (4.17% in ethanol); MR_{found} 55.33; $C_{12}H_{18}O_2$ F_1, 3-membered ring, MR_{calc} 55.10. The presence of 1 double bond in the molecule was established by titration with perphthalic acid. Saponification of the product with aqueous-alcoholic alkali (4.5%) gave an alcohol with the constants: b.p. 69-72°/2.5 mm; $n^{20}D$ 1.4953, d^{20}_4 0.9660, $[\alpha]_D$ = − 41.37° (4.84% in ethanol); MR_{found} 45.91, $C_{10}H_{16}O$ F_1, 3-membered ring, MR_{calc} 45.73; 3,5-dinitrobenzoate, m.p. 106-107°. The alcohol rapidly crystallized when seeded with the crystalline product from the saponification of the $C_{12}H_{18}O_2$ acetate obtained in one of the experiments by purification through the 3,5-dinitrobenzoate (b.p. 100-103°/9 mm; m.p. 55-56°).

On the basis of the "onium" mechanism of the reaction of Δ^3-carene oxide with acetic anhydride, it is possible to represent the formation of two acetates of bicyclic alcohols as follows:



D. Tishchenko, A. Khovanskaia and T. Danilova [11] assigned structure (II) to the acetate of carenol, which they obtained from 3-chloro-Δ^4-carene by the action of potassium acetate. The acetate of carenol and the acetate from the Δ^3-carene oxide differ considerably in $n^{20}D$ (1.4820 and 1.4746). The alcohols – products of alkaline saponification – had the constants: carenol, b.p. 80-81°/0.7 mm, $n^{20}D$ 1.4987, d^{20}_4 0.967. The alcohol from Δ-carene oxide: b.p. 69-72°/2.5 mm, $n^{20}D$ 1.4957, d^{20}_4 0.9660.

Treatment of the alcohol from Δ^3-carene oxide: with phenyl isocyanate gave two products: 1) with a m.p. of 96-97° and 2) with a m.p. of 106-107°, the latter compound being obtained in the lesser amount. Study of the reaction products is in progress.

LITERATURE CITED

[1] A. Kergomard and M. Th. Geneix, Bull. Soc. Chim., 1958, 390.

[2] A. Kergomard, J. Philibert-Bigo, Bull. Soc. Chim., 1958, 393.

[3] B. A. Arbuzov and Z. G. Isaeva, J. Gen. Chem., 24, 1250 (1954). *

[4] R. Johnston and J. Read, J. Chem. Soc. 1934, 233.

[5] D. Tishchenko and V. Foliadov, J. Gen. Chem., 20, 905 (1950). *

[6] Z. G. Isaeva and B. A. Arbuzov, J. Gen. Chem., 19, 884, 893 (1949).*

[7] G. O. Schenk, H. Eggert, W. Denk, Lieb. Ann., 584, 177 (1953).

[8] H. Schmidt. Ber., 63, 1129 (1930).

[9] H. Schmidt. Ber., 77 B, 167 (1944); Chem. Abstr., 39, 2983 (2) (1945).

[10] R. H. Reitsema, Lieb. Ann., 75, 1996 (1953).

[11] D. Tishchenko, A. Khovanskaia and T. Danilova, J. Gen. Chem., 22, 803 (1952). *

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THE SYNTHESIS OF RACEMIC TUBOCURARINE

V. G. Voronin, O. N., Tolkachev and N. A. Preobrazhenskii

(Presented by Academician A. N. Nesmeianov, April 30, 1958)

The active principles of tube curare are alkaloids of the bisbenzyltetrahydroisoquinoline group of unsymmetrical structure, and they differ from each other in the degree of methylation of the nitrogens and phenolic hydroxyls. Among the secondary tertiary bases are L-chondrofoline, D- and L-curine, and certain others. The major representative of the quaternary ammonium salts is D-tubocurarine hydrochloride (tubocurarine, curarine) (X), which has a high physiological activity, causing relaxation of the striated muscles.

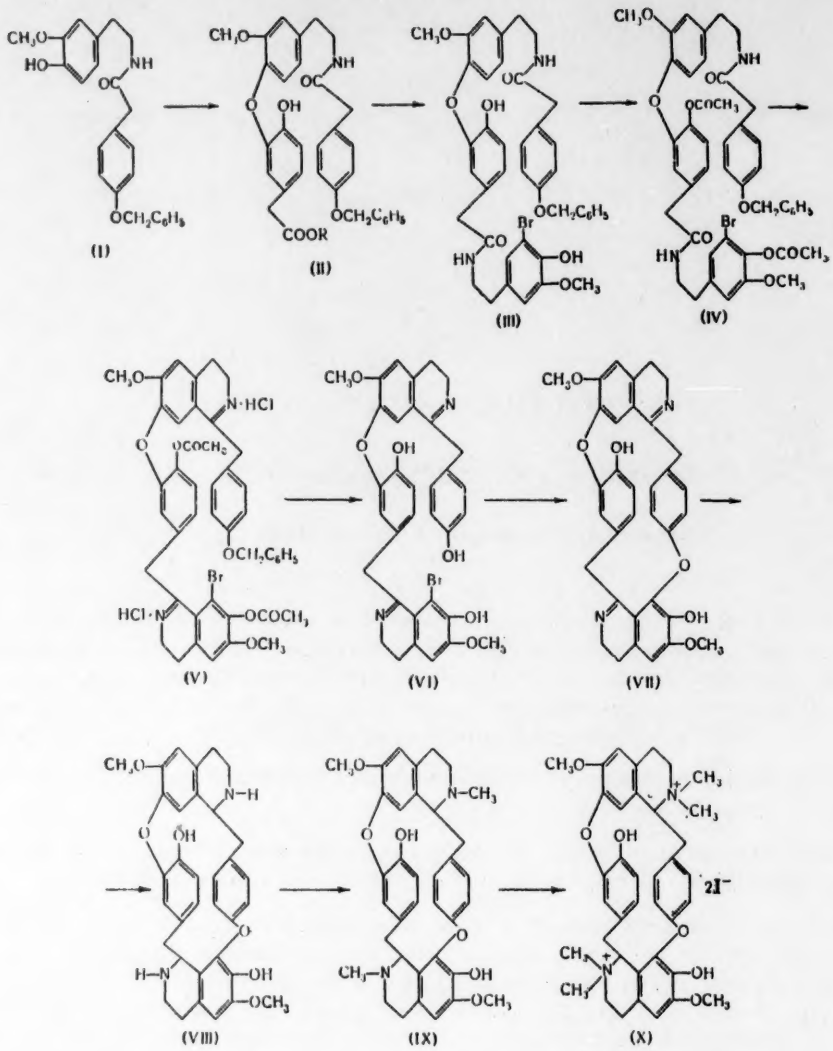
Up to the present, the structure of tubocurarine remains unconfirmed by synthesis, although there has been considerable work along this line.

The basis of our synthesis for phenolic alkaloids of the chondodendrine group is the successive building up of a system containing the elements of the natural alkaloid (see scheme on page 646).

Condensation of the β-(3-methoxy-4-hydroxyphenyl)ethylamine, m.p. 156-157°, with 4-benzyloxyphenylacetic acid, m.p. 120-121°, led to the formation of the β-(3-methoxy-4-hydroxyphenyl)ethylamide of 4'-benzyloxyphenylacetic acid (I), m.p. 121-122°. By the action of the ethyl ester of 3-bromo-4-hydroxyphenylacetic acid, m.p. 36-36.5°, compound (I) was converted to the β-[3-methoxy-4-(2"-hydroxy-5"-carbethoxymethylphenoxy)phenyl] ethylamide of 4'benzyloxyphenylacetic acid ((II), R=C_2H_5), m.p. 65-67°, which, on saponification, gave the corresponding acid ((II), R=H), m.p. 83.5-85°. Interaction of the latter with β-(3-methoxy-4-hydroxy-5-bromophenyl)ethylamine, m.p. 169-170°, formed the β-{3-methoxy-4-[2"-hydroxy-5"-(3'''-methoxy-4'''-hydroxy-5'''-bromophenyl, ethyl carbamidomethyl)phenoxy]phenyl} ethylamide of 4'-benzyloxyphenylacetic acid (III), m.p. 119.5-120.5°. The phenolic hydroxyls in diamide (III) were protected by acetylation, and the diacetyl derivative (IV) was subjected to the Bischler-Napieralski reaction with phosphoryl chloride in chloroform. The resulting 1-(4'-benzyloxybenzyl)-6-methoxy-7-[2"-acetoxy-5"-(6'''-methoxy-7'''-acetoxy-8'''-bromo-3''',4'''-dihydroisoquinolyl-1'''-methyl)phenoxy]-3,4-dihydroisoquinoline dihydrochloride (V) was saponified with 20% hydrochloric acid to 1-(4'hydroxybenzyl)-6-methoxy-7-[2"-hydroxy-5"-(6'''-methoxy-7'''-hydroxy-8'''-bromo-3''',4'''-dihydroisoquinolyl-1'''-methyl)phenoxy]-3,4-dihydroisoquinoline (VI), m.p. 174-180°. The concluding stage was the formation of the macrocyclic system by completion of the second ether bond to give the compound of structure (VII), m.p. of the hydrochloride 176-180°. By subsequent reduction, we were able to obtain three isomers of norchondrofoline (VIII):

1. Hydrochloride m.p. 174-176° (from an alcohol-ether mixture, 1:1), Base m.p., 132-134°.

Found % C 72.04; H 5.9; N 4.98; 4.92 $C_{34}H_{34}O_6H_2$. Calculated % C 72.00; H 6.01; N 4.94.



2. Hydrochloride m.p. 194-196.5° (from an alcohol-ether mixture, 1:1).

Found %: C 62.3; H 6.54; N 4.44 $C_{34}H_{34}O_6H_2 \cdot 2HCl \cdot H_2O$. Calculated %: C 62.2; H 5.82; N 4.28.

3. Hydrochloride m.p. 185-187.5° (from an acetone-ether mixture, 1:1).

Found %: C 63.25; H 6.59; N 4.54 $C_{34}H_{34}O_6N_2 \cdot 2HCl \cdot \frac{1}{2}H_2O$. Calculated %: C 63.1; H 5.72; N 4.33.

The first two of these were converted by methylation to the bitertiary bases corresponding in composition to chondodendrine (IX):

1. M. p. 207.5-110.5° *

Found %: C 71.2; 71.2; H 6.61; 6.70; N 4.69; 4.38 $C_{36}H_{38}O_6N_2 \cdot \frac{1}{2}H_2O$. Calculated %: C 71.6; H 6.5; N 4.65.

2. M. p. 128-130.5°. *

Treatment of each of these bases with methyl iodide and subsequent crystallization gave four methiodides which were identical with respect to chemical composition (X):

*As in original — Publisher's note.

1. M.p. 164-166.5° (from acetone-ether mixture, 1:2).

Found %: N 3.43 $C_{38}H_{44}O_6N_2I_2$. Calculated %: N 3.19.

2. M. p. 189-190.5° (from alcohol).

Found %: C 52.2; 52.15; H 5.05; 5.14 N 3.20; 3.18 $C_{38}H_{44}O_6N_2I_2$. Calculated %: C 52.00; H 5.05; N 3.19.

3. M. p. 210-212° (from alcohol).

Found % C 52.5; H 5.23; N 3.08; 3.17. $C_{38}H_{44}O_6N_2I_2$. Calculated %: C 52.00; H 5.05; N 3.19.

4. M.p. 257-260.5° (from water).

λ_{max}(alcohol) 225, 280 mμ (log ε 4.5488; 4.0832); λ_{min} 260 mμ (log ε 4.0425).

λ_{max}(0.05 N KOH) 225, 295 mμ (log ε 4.763; 4.225); λ_{min} 280 mμ (log ε 4.1715).

Found % C 52.33; 52.29; H 4.94; 5.20; N 2.97; 3.12 $C_{38}H_{44}O_6N_2I_2$. Calculated %: C 52.00; H 5.05; N 3.19.

The fourth of these salts has a melting point close to that of natural D-tubocurarine iodide (m.p. 263-265°), and a mixed melting point showed no depression. The ultraviolet spectrum of this compound agreed with the spectrum of D-tubocurarine iodide, and the shifting of the curve as a function of pH was the same.

Thus, the synthetic compound can be considered to be the racemate of the natural alkaloid.

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CONTRIBUTION TO THE PROBLEM OF THE STEREOCHEMISTRY OF VANADYL INNER-COMPLEX COMPOUNDS

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In the present communication, we shall dwell on some questions of the stereochemistry of vanadyl inner-complex compounds with azomethine derivatives of aromatic o-hydroxyaldehydes.

The first inner-complex compounds of the vanadyl group with azomethine derivatives were synthesized by Pfeiffer and co-workers [1]. Later, Mukherjee and Ray [2] prepared three complex compounds of VO^{2+} with salicylaldimino acids and studied their magnetic susceptibility; the complexes were formed with salicylalinine (M_{eff} = = 1.78 M_B), salicylglycine (μ_{eff} = 1.80 M_B), and salicylanthranilic acid (μ_{eff} = 1.81 M_B). Considering that the oxygen occupies two coordination sites, they proposed that the vanadium in these compounds has a coordination number of six and that the bond configuration corresponds to d^2sp^3.

It has been established experimentally that the magnetic moment of vanadyl complex compounds does not depend on the coordination number of the central atom. For example, as shown by Bayer, Bielig and Hausser [3, 4], in vanadyl disalicylalethylenediiminate [oxosalicylaldehyde-ethylenediimine-vanadium (IV)] (μ_{eff} = 1.70 – 1.72 μ_B) the coordination number is five, while in the o-oxyquinolate vanadyl compound [oxo-di(8-oxyquinolino)pyridine-vanadium(IV)] (μ_{eff} = 1.75 μ_B) it is six owing to the coordinatively added pyridine. This is in good agreement with theoretical considerations to the effect that regardless of the coordination number of the central atoms, the effective magnetic moment of vanadyl complexes is 1.73 μ_B. Nevertheless, by comparing the magnetic moment with analytical data, it is possible to form specific conclusions as to the stereochemistry of vanadyl inner-complex compounds.

Except for vanadyl 5-bromo-2-oxybenzalanalinate [oxo-benzaldehyde-aniline-vanadium (IV)], the inner-complex compounds were synthesized by heating stoichiometric amounts of vanadyl chloride and aldehyde in an alcoholic medium and subsequently adding a slight excess of aqueous solutions of ethylenediamine or ammonia. The vanadyl 5-bromo-2-oxybenzalanilinate was prepared by heating for an hour alcoholic solutions of 5-bromo-2-hydroxybenzalaniline and vanadyl chloride in a mole ratio of 2:1.

TABLE 1

Compound	Found, %				Calculated, %			
	V	N	C	H	V	N	C	H
Vanadyl 5-bromo-2-oxybenzalanilinate $(C_{13}H_9ONBr)_2VO$	8,42	4,45; 4,62	51,09; 49,98	3,06; 2,73	8,25	4,54	50,57	2,94
Vanadyl di(5-bromo-2-oxybenzal)ethylenediiminate $(C_8H_6ONBr)_2VO$	10,50; 10,49	5,70; 6,03	39,24; 38,84	2,57; 2,50	10,37	5,72	39,13	2,46
Vanadyl 5-bromo-2-oxybenzaliminate $(C_7H_5ONBr)_2VO$	10,81	6,15	—	—	10,94	6,03	—	—

The resulting crystalline materials, which were colored various hues of green, were dried to constant weight and analyzed.

The magnetic susceptibility was determined by the method of Gouy; the determinations were carried out at room temperature. Moore's salt, repeatedly recrystallized, served as the standard. The diamagnetic susceptibility of V^{4+} was taken as $9.2 \cdot 10^{-6}$ [8]. The correction for the diamagnetism of the organic portion of the inner-complex compounds was calculated from Pascal's constants. As seen from Table 2, the magnetic moments of the complex compounds lay in the range 1.76-1.80 M_B. The chemical analyses convinced us that our complex compounds did not contain solvent, particularly water, which could be coordinated to the vanadium atom.

TABLE 2

Compound	$\chi T \cdot g \cdot 10^6$	χ, (g.-ion V^{4+})$\cdot 10^6$	Temp. °K	$\mu_{eff.} \cdot \mu_B$
Vanadyl 5-bromo-2-oxybenzalanilinate	1.76	1370	294	1.80
Vanadyl di(5-bromo-2-oxybenzal)ethylenediiminate	2.22	1290	294	1.76
Vanadyl 5-bromo-2-oxybenzaliminate	2.44	1335	295	1.78

Since, as a rule, the oxygen atom occupies one coordination site, vanadium has a coordination number of five in these compounds, and not six as proposed by Mukherjee and Ray [2].

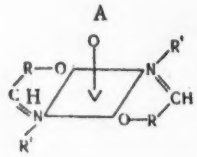
Recently, George and Irving [5] proposed that vanadium porphyrin and phthalocyanine complexes must have the configuration of a square pyramid. According to Kimball [6], a square pyramid corresponds to d^2sp^2 or dsp^3 hybridization, which can apply in the present case.

But according to Lesnik's ideas [7], d^2sp^2 hybridization corresponds to a tetragonal pyramid with the central atom lying in the plane of the base and having one bond normal to this plane, while dsp^3 hybridization presumes that the central atom lies inside the pyramid along its altitude. The supposition that the vanadium ion lies in the plane of the base of a tetragonal pyramid is apparently hypothetical. That in vanadyl o-oxyquinolinate [oxo-di(8-oxyquinilino)pyridine-vanadium(IV)] [4] the pyridine molecule is coordinated with the central ion is confirmation of this. The unshared pair of electrons of the nitrogen atom in the pyridine molecule occupies an unbonded 4p orbital, and the square pyramid is readily completed to an octahedron.

On the basis of the above, we may propose that these inner-complex compounds of the vanadyl group with azomethine derivatives of o-hydroxyaldehydes have a square pyramidal structure. The σ-bonds in this case are formed as a result of d^2sp^2-hybridization. Moreover, one 3d orbital of the vanadium participates in the formation of a stable π-bond with the oxygen atom.

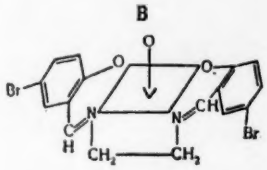
The structures of these compounds can be depicted by formulas A and B.

A



where I R=Br-C_6H_3; R'=C_6H_5
III R=Br-C_6H_3; R'=H

B



LITERATURE CITED

[1] P. Pfeiffer, T. Hesse et al., J. Prakt. Chem., 149, 217 (1937).

[2] A. K. Mukherjee, P. Ray, J. Indian Chem. Soc., 32, 505 (1955).

[3] E. Bayer, H. J. Bielig, K. H. Hausser, Lieb. Ann., 584, 116 (1953).

[4] H. J. Bielig, E. Bayer, Lieb. Ann., 580, 135 (1953).

[5] P. George, D. H. Irving, Nature, 173, 1148 (1954).

[6] G. E. Kimball, J. Chem. Phys., 8, 188 (1940).

[7] A. G. Lesnik, J. Phys. Chem., 22, 541 (1948).

[8] A. V. Jagannadham, Proc. Rajstan Acad. Sci., 1, 6 (1950); Chem. Abstr. 45, 9948 (1951).

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SYNTHESIS OF POLYENIC ALDEHYDES AND KETONES BY CONDENSATION OF ALDEHYDIC ACETALS WITH VINYL AND ISOPROPENYL ETHERS

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Polyenic aldehydes and ketones are widely known. Some of them (citral, farnesal) are encountered in nature; others are intermediate products in the synthesis of isoprenoids, the investigation of which has been the subject of a series of communications from our laboratory [1]. Considerably less attention has been given to the investigation and synthesis of polyenic carbonyl compounds of unbranched structure, although they can occur as stages in the synthesis of such important natural substances as fatty acids and sugars.

Practically the only method for the preparation of polyenic aldehydes of unbranched structure is by the polycondensation of aldehydes. Thus, by the condensation of acetaldehyde with crotonaldehyde (or by the polycondensation of crotonaldehyde itself) in the presence of secondary amines, Kuhn and also Fischer [2] obtained a mixture of polyenic aldehydes, both cyclic and with an open chain, together with a significant amount of high-molecular-weight products. The separation of this mixture presented great difficulty, the more so since the highly unsaturated aldehydes were extremely sensitive to atmospheric oxygen and to heating. Attempts to carry out the reaction selectively [3] were unsuccessful – the yield of polyenic aldehydes comprised not more than 20%.

The aim of the present work was the extension of the condensation of acetals with vinyl ethers [4] to the preparation of polyenic aldehydes and ketones with a straight carbon chain.

The condensation of the acetal of crotonaldehyde (I) with vinyl ethyl ether in the presence of zinc chloride gave the acetal of 3-ethoxy-4-hexenal (II), which, on hydrolysis, gave sorbaldehyde (III). This reaction can be carried out in a single stage without the isolation of acetal (II), and the yield of sorbaldehyde in this case amounts to 75%. Sorbaldehyde (III), after conversion to the acetal (IV), can be introduced into a succeeding condensation with vinyl ethyl ether, and, after hydrolysis, 2,4,6-octatrienal (V) is obtained in a yield of 71%. 2,4,6,8-Decatetraenal (VI) and 2,4,6,8,10-dodecapentaenal (VII) were synthesized by such successive building up of the chain. The intermediate acetals were obtained in high yield by the action of tetraethoxysilane on the aldehydes according to the method developed previously in our laboratory [5].

$$CH_3CH=CHCH(OC_2H_5)_2\ (I) \xrightarrow{CH_2=CHOC_2H_5}$$
$$\rightarrow CH_3CH=CHCH(OC_2H_5)CH_2CH(OC_2H_5)_2\ (II) \rightarrow$$
$$\xrightarrow{H^+} CH_3(CH=CH)_2CHO\ (III) \xrightarrow{Si(OC_2H_5)_4} CH_3(CH=CH)_2CH(OC_2H_5)_2\ (IV) \rightarrow$$
$$\rightarrow CH_3(CH=CH)_3CHO\ (V) \rightarrow CH_3(CH=CH)_4CHO\ (VI) \rightarrow CH_3(CH=CH)_5CHO\ (VII)$$

All stages proceed with high yields (70-80%); thus, this method has definite advantages over the method of Kuhn.

It was found that isopropenyl ethyl ether also reacts with acetals in a manner similar to that of vinyl ethyl ether, and this opened up a new route for the synthesis of polyenic ketones. Thus, the condensation of the acetal of crotonaldehyde (I) with isopropenyl ethyl ether leads to the acetal of 4-ethoxy-5-heptene-2-one (VIII), which, after hydrolysis, gives 3,5-heptadiene-2-one (IX) with a yield of 51%. This route was used to synthesize 3,5,7-nonatriene-2-one (X) and 3,5,7,9-undecatetraene-2-one (XI) from the acetals of sorbaldehyde and 2,4,6-octatrienal.

$$CH_3CH = CHCH(OC_2H_5)_2\ (I) \xrightarrow{CH_2=C(CH_3)OC_2H_5}$$

$$\rightarrow CH_3CH = CHCH(OC_2H_5)CH_2C(OC_2H_5)_2CH_3\ (VIII) \rightarrow$$

$$\xrightarrow[51\%]{H^+} CH_3(CH = CH)_2COCH_3\ (IX)$$

$$CH_3(CH = CH)_2CH(OC_2H_5)_2(IV) \xrightarrow[62\%]{} CH_3(CH = CH)_3COCH_3\ (X)$$

$$CH_3(CH = CH)_3CH(OC_2H_5)_2 \xrightarrow[64\%]{} CH_3(CH = CH)_4COCH_3\ (XI)$$

The structures of the polyenic ketones were proved by hydrogenation to the corresponding saturated ketones, which were identified by means of their derivatives.

EXPERIMENTAL

A freshly prepared 10% solution of zinc chloride in ethyl acetate was used in all condensation experiments. Hydrolysis of the ethoxyacetals and distillation and crystallization of the polyenic compounds were carried out in an atmosphere of nitrogen.

Condensation of the acetal of crotonaldehyde (I) with vinyl ethyl ether. To a mixture of 31 g of the acetal of crotonaldehyde (I) and 5 ml of zinc chloride solution was added, with stirring, 16 g of vinyl ethyl ether; the addition was carried out at a rate such that the temperature of the reaction mixture did not rise above 45°. After the addition of the ether, the reaction mixture was stirred for about an hour; the temperature was then raised to 50-60°, and the stirring was continued for another 1.5 hours. The reaction products were diluted with an equal volume of ether, washed with a 5% sodium hydroxide solution, and dried over calcined potassium carbonate. Distillation gave 37.2 g (79% of theoretical) of the acetal of 3-ethoxy-4-hexenal (II); b.p. 95-100°/12 mm, n_D^{20} 1.4248; d_4^{20}, 0.8908.

Found % C 66.61; 66.68; H 11.24; 11.11 $C_{12}H_{24}O_3$. Calculated %: C 66.64; H 11.14.

Preparation of sorbaldehyde (III). 22 g of acetal (II) and 45 ml of a mixture prepared from 80 ml of acetic acid, 22 g of anhydrous sodium acetate, and 13 ml of water were heated with stirring in an atmosphere of nitrogen at 85-90° for 3.5-4 hours. The mixture was cooled and poured into 150 ml of ice water; the upper layer was separated, and the aqueous layer was extracted with ether. The ether and most of the acetic acid were distilled under vacuum; the residue was carefully neutralized by agitation with a solution of sodium bicarbonate, and, after the neutralized residue had been dried, distillation gave 8.1 g (83% of theoretical) of sorbaldehyde with a b.p. of 65-67°/15 mm and $n^{20}D$ 1.5354. λ_{max} (in ethanol) 271.5 $m\mu$.

When the condensation and hydrolysis were carried out successively without isolation of the intermediate acetal (II), the overall yield of sorbaldehyde amounted to 75%.

Acetal of sorbaldehyde (IV). A mixture of 96 g of sorbaldehyde (III), 260 g (25% excess) of tetraethoxysilane, 32 ml of absolute alcohol, and 6 ml of 85% phosphoric acid were allowed to stand for 3 days in a sealed vessel at 20°. The resulting reaction mixture was vigorously agitated in a separatory funnel with 1 liter of 30% sodium hydroxide solution for 10-15 minutes; the upper layer was separated, and the aqueous layer was extracted with ether. The ether extract was combined with the main product, the mixture was washed with water, dried with potassium carbonate, and distilled. 144 g (85%) of theoretical) of the acetal of sorbaldehyde (IV) was obtained; b.p. 99-100°/21 mm, $n^{17}D$ 1.4560; d^{20}_4 0.8831.

Found %: C 70.49; 70.61; H 10.60; 10.60 $C_{10}H_{18}O_2$. Calculated %: C 70.50; H 10.66.

Preparation of 2,4,6-octatrienal (V). 28.8 ml of vinyl ethyl ether was added, under the conditions described for the preparation of acetal (II), to a mixture of 58 g of acetal (IV) and 11 ml of zinc chloride solution. After completion of the reaction, 32.8 g of anhydrous sodium acetate, 275 ml of acetic acid, and 25 ml of water were added to the product, and the mixture was heated in a stream of nitrogen at 90-95° for an hour. After the usual treatment and distillation, 34.4 g (71% of theoretical) of 2,4,6-octatrienal (V) was obtained; b.p. 64-69°/0.4 mm, m.p. 57-58° (from petroleum ether), which corresponds to the literature value [2]. The 2,4-dinitrophenylhydrazone melted at 188-189° (from methanol-ethyl acetate). λ_{max} (in isooctane) 370.5; 389 and 404 $m\mu$ [3].

Preparation of 2,4,6,8-decatetraenal (VI). By the above-described method, from 34 g of aldehyde (V) was obtained 47.6 g (87% of theoretical) of the acetal; b.p. 130-132° / 15 mm, 74-76° / 0.2 mm, $n^{20}D$ 1.5031; d^{20}_4 0.8971.

Found %: C 73.03; 73.07; H 10.40; 10.31. $C_{12}H_{20}O_2$. Calculated %: C 73.41; H 10.27.

Condensation, under the above-described conditions, of 19.6 g of this acetal with vinyl ethyl ether and hydrolysis of the reaction product by heating with sodium acetate, acetic acid, and water for 10-15 minutes at 75-80° gave 12.2 g (83% of theoretical) of 2,4,6,8-decatetraenal (VI); b.p. 112-116° / 0.4 mm, m.p. 109-109.5° (from petroleum ether), which agrees with the literature value [6].

Preparation of 2,4,6,8,10-dodecapentaenal (VII). 13.2 g (72% of theoretical) of the acetal, b.p. 104-107° / 0.1 mm, $n^{20}D$ 1.5205. was prepared by the above-described method from 12 g of aldehyde (VI).

Found %: C 75.60; 75.67; H 10.0; 10.0 $C_{14}H_{22}O_2$. Calculated %: C 75.59; H 9.97.

Condensation of 6.7 g of this acetal with vinyl ethyl ether and subsequent hydrolysis of the reaction product gave 3.7 g (72% of theoretical) of 2,4,6,8,10-dodecapentaenal (VII); m.p. 159-161° (from methanol) [2].

Condensation of the acetal of crotonaldehyde with isopropenyl ethyl ether. The condensation was carried out similarly to that of the preparation of acetal (II) with the exception of the heating at the completion of the reaction. 17 g of acetal (I) gave 15.5 g of 2,4,4-triethoxy-5-heptene (VIII) with a b.p. of 57-61° / 0.1 mm and $n^{18}D$ 1.4300, hydrolysis of this product with a mixture of sodium acetate, acetic acid, and water (4 hours, 85-90°) gave 6.8 g (51% of theoretical) of 3,5-heptadiene-2-one (IX) with a b.p. of 79-80° / 18 mm and $n^{20}D$ 1.5182.

Found %: C 76.50; 76.59; H 9.08; 9.17 $C_7H_{10}O$. Calculated %: C 76.38; H 9.15.

Preparation of 3,5,7-nonatriene-2-one (X). In a similar manner, condensation of 8.5 g of the acetal of sorbaldehyde (IV) with isopropenyl ethyl ether and hydrolysis of the reaction product (1 hour, 80-90°) gave 4.2 g (62% of theoretical) of 3,5,7-nonatriene-2-one (X): b.p. 62-64° / 0.2 mm, $n^{20}D$ 1.5453. λ_{max} (in ethanol) 229.5 (log ϵ 4.05) and 316 (log ϵ 4.23) mμ.

Its 2,4-dinitrophenylhydrazone melted at 170-172° (from ethanol-ethyl acetate); λ_{max} (in isooctane) 316 and 404 mμ.

Found %: C 56.52; 56.53; H 5.02; 4.97; N 18.26; 18.29 $C_{15}H_{16}O_4N_4$. Calculated %: C 56.93; H 5.10; N 17.72.

3 moles of hydrogen were absorbed during exhaustive hydrogenation of ketone (X), and 2-nonanone was obtained; the semicarbazone of the 2-nonanone melted at 120-120.5° (from methanol), which is in agreement with the literature value [7].

Preparation of 3,5,7,9-undecatetraene-2-one (XI). In a manner similar to that described above, from 9.8 g of the acetal of 2,4,6-octatrienal was obtained 5.2 g (64% of theoretical) of 3,5,7,9-undecatriene-2-one (XI); b.p. 94-96° / 0.4 mm, m.p. 101-103° (from petroleum ether) [8]. λ_{max} (in ethanol) 243.5 (log ϵ 3.85) and 351 (log ϵ 4.62) mμ.

The 2,4-dinitrophenylhydrazone prepared from this ketone melted at 163-164° (from methanol-ethyl acetate).

Found %: N 16.67; 16.72 $C_{17}H_{18}O_4N_4$. Calculated %: N 16.37.

4 moles of hydrogen were absorbed during exhaustive hydrogenation of ketone (XI), and 2-undecanone was obtained; the semicarbazone of this ketone melted at 122-123.5° (from aqueous methanol) [7].

LITERATURE CITED

[1] I. N. Nazarov et al., Proc. Acad. Sci. USSR, 114, 331, 1029 (1957); *I. N. Nazarov and Zh. A. Krasnaia, Proc. Acad. Sci. USSR, 118, 716 (1958).

[2] R. Kuhn, M. Hoffer, Ber., 63, 2164 (1930); F. G. Fischer, K. Hultzsch, W. Flaig, Ber., 70, 370 (1937).

[3] I. N. Nazarov and Zh. A. Krasnaia, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1958, 238.*

*Original Russian pagination. See C. B. translation.

[4] R. J. Hoaglin, D. H. Hirsch, J. Am. Chem. Soc., 71, 3468 (1949); O. Isler et al., Helv. Chim. Acta, 39, 249, 259 (1956).

[5] I. N. Nazarov, S. M. Makin and B. K. Kruptsov, Proc. Acad. Sci. USSR, 117, 823 (1957). *

[6] F. G. Fischer, O. Wiedemann, Lieb. Ann., 513, 251 (1934).

[7] A. Haller, A. Lassieur, C. R., 150, 1013 (1910).

[8] F. G. Fischer, H. Schulze, Ber., 75 B, 1467 (1942).

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CHEMISORPTION OF ISOPROPYL ALCOHOL ON CATALYSTS – FERROALUMINA GELS

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(Presented by Academician A. A. Balandin, April 19, 1958)

The decomposition of isopropyl alcohol is frequently used as a standard in characterizing the activity and selectivity of oxide catalysts. This reaction can follow two courses: dehydration (for example, on Al_2O_3) and dehydrogenation (for example, on metals or oxides such as Fe_2O_3). A detailed investigation of ferroalumina gels, which will be the subject of another communication, has been carried out in our laboratory. It was, therefore, of interest to investigate the adsorption of isopropyl alcohol on $Fe_2O_3 \cdot Al_2O_3$ catalysts prepared during the course of the work; both of the reactions proceed over these catalysts. The investigation was carried out by the vacuum method at 30° using a McBain balance. The initial samples were prepared by coprecipitation of $Al(OH)_3$ and $Fe(OH)_3$ with a 10% aqueous solution of NH_4OH. The resulting precipitate was washed, dried, and formed into tablets (1.2-1.3-mm diameter). Individual portions of these catalysts were heated for 7 hours at 400 and 600°. Prior to the experiments, the samples were heated to 300° under a pressure of 10^{-5}mm Hg. Weighed portions of these same samples were treated similarly, and were then calcined in air at 1250° in a crucible furnace in order to determine the loss in weight. The loss in weight represented the structural water removed during the calcination, and the amounts removed are shown in Table 1.

TABLE 1

Content of Fe_2O_3, mole %	8	18	32	40	46	57
Content of H_2O, wt. %						
at 400°	5,1	3,5	2,6	2,2	2,13	1,93
at 600°	1,3	1,2	—	0,9	—	0,7

TABLE 2

	Content of Fe_2O_3, mole %											
	8		18		32		40		46		57	
Temp. of treatment, °C	400	600	400	600	400	600	400	600	400	600	400	600
Specific Surface, s, sq. m/g.	360	215	350	200	320	160	280	150	270	160	260	120
Conc. of OH groups, μ equiv/sq. m	15,6	6,7	11,1	6,6	9,0	—	8,8	6,8	8,8	—	8,2	4,9
Amt. chemisorbed, a_x, mol/sq. m	3,5	4,5	3,5	4,9	3,8	4,4	4,3	4,3	4,0	4,1	4,2	4,0
Area, ω_0, sq. A	48	39	49	37	45	40	41	41	45	42	43	42

Since the molecular areas and the behavior of $i\text{-}C_3H_7OH$ on these catalysts were unknown, the values of the specific surface of the samples were determined by the BET method from the adsorption isotherms of benzene vapors at 20° assuming the area occupied by one benzene molecule in a close-packed monolayer to be 41 sq. A.

The pore diameters and total pore volumes of each of the samples were calculated from the isotherms. The measurements showed that all of the samples investigated had comparatively wide pores of the order of 60-100 A; the samples containing 8 and 46 mole % Fe_2O_3 and calcined at 400° were exceptions, the pore diameter being somewhat less – about 50 A. Values of the specific surface are presented in Table 2.

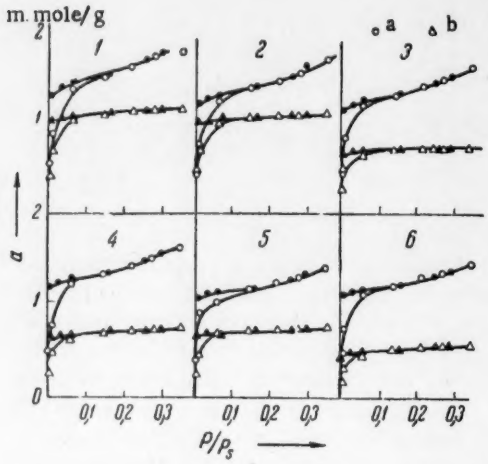


Fig. 1. Sorption isotherms for isopropyl alcohol on Fe_2O_3/Al_2O_3 catalysts. Fe_2O_3 content of catalysts (in mole %): 1 – 8, 2 – 18, 3 – 32, 4 – 40, 5 – 46, 6 – 57. Calcination temperature: a – 400°,

The effects of catalyst composition and heat treatment of the catalyst were investigated in experiments with absolute i-C_3H_7OH. Figure 1 presents the experimentally-determined isotherms for the adsorption and desorption of i-C_3H_7OH on catalysts with various ratios of Fe_2O_3 to Al_2O_3 calcined at 400 and 600°. The solid points denote desorption. It is seen from Figure 1 that at 30°, isopropyl alcohol was chemisorbed on the surfaces of all of the catalysts investigated. Catalyst composition had little effect on the amount of chemisorption, which depended much more on the specific surface of the catalyst. This indicates that either there is only one component in the surface layer of the catalyst, or else both components chemisorb isopropyl alchol to the same extent. However, the first assumption is untenable, since the catalysts were prepared by co-precipitation. The second assumption was confirmed by phase-analysis data, which showed that the catalyst components were dissolved in each other forming two solid solution phases: 1) up to 8 mole % Fe_2O_3 in Al_2O_3 and 2) up to 25 mole % Al_2O_3 in Fe_2O_3. Figure 1 also shows that an increase in the calcination temperature of the catalysts leads to a decrease in both the total adsorption and the chemisorption of i-C_3H_7OH. The latter circumstance must be considered when explaining the nature of the chemisorption, since with more severe heat treatment, a) there is a decrease in the water content, and b) the specific surface of each catalyst decreases. It is necessary to consider the question, on which of the surface groups does chemisorption occur ?

In 1950, Kiselev and co-workers[1] observed the irreversible adsorption of CH_3OH on silica gel due to the formation of a surface ether. The work of Topchieva and Ballod [2] established that in the interaction of methyl alcohol with aluminum oxide and aluminosilicate catalysts, analogous surface compounds are formed by reaction with the surface hydroxyl groups according to: $CH_3OH + H-O-Al \rightleftharpoons H_2O + CH_3-O-Al$.

Terenin and co-workers [3,4] and later Babushkin and co-workers [5,6], through an investigation of the infrared spectra of substances adsorbed on glasses, silica gel, and aluminum oxide, showed that during the adsorption of alcohols there is a disappearance of frequencies characteristic of undisturbed hydroxyl groups and the appearance of frequencies characteristic of the C–O–M bond in bulk alcoholates. The optical methods also disclosed the formation of a surface complex through hydrogen bonding M–O–H. In the case investigated by us, the strong adsorp-

H–O–R

tion of i-C_3H_7OH indicates the formation of a surface alcoholate of the type R–O–Me, which under catalysis conditions (at an elevated temperature) can decompose to give propylene.

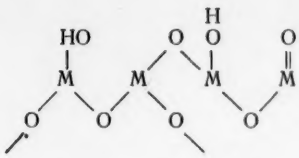
Thus, it can be concluded that chemical adsorption of isopropyl alcohol proceeds on the surface of the catalysts with the formation of surface alcoholates.

In considering the mechanism of the chemisorption of isopropyl alcohol, we started with the assumption that hydroxyl groups project from the surface of the catalyst. It is evident that the concentration of OH groups on the surface depends on the bulk composition and on the heat treatment. It is seen from Table 1 that the water content of the catalyst decreases with an increase in calcination temperature and with an increase in the

Fe_2O_3 content, the water content decreasing more rapidly than the specific surface (cf. Tables 1 and 2). This indicates that the concentration of OH groups per unit of catalyst surface decreases with these changes. It would seem that there must be an accompanying decrease in the amount of chemisorption. From the desorption kinetics, we evaluated the chemisorption as that part of the sorbed alcohol which was not desorbed over a period of 2 hours when the samples were evacuated to a pressure of $5 \cdot 10^{-5}$ mm Hg at room temperature. This amount was calculated per unit of surface in order to exclude the factor of the very large surface which changed both with the heat treatment and with a change in the Fe_2O_3 content of the catalyst.

In Table 2 are presented the values of the chemisorption per unit surface (a_x) and the values for the concentration of OH groups, the latter being calculated on the basis of the assumption that all of the water on the surface is in the form of OH groups. This table also includes the values of ω_0, the area of the catalyst surface occupied by a molecule of isopropyl alcohol in a monolayer. These values were calculated by the equation $\omega_0 = \frac{s}{a_m N}$, where s is the specific surface of the catalyst determined by the BET method from the adsorption isotherm of benzene vapor, N is Avagadro's number, and a_m is the volume of a monolayer of isopropyl alcohol calculated by the BET equation using the desorption branch of the isotherm for $i\text{-}C_3H_7OH$.

It is seen from Table 2 that the amount of chemisorbed isopropyl alcohol remained practically constant at about 4 μmoles/sq. m, and, to a first approximation, did not depend on catalyst composition nor on the heat treatment. Similarly, the concentration of OH groups on samples calcined at 600° did not depend on catalyst composition, and was 6.7 μ equiv./sq.m. At the same time, for samples heated at 400°, this concentration decreased with an increase in the Fe_2O_3 content, and was greater than for similar samples heated at 600°. This probably indicates that there is a sufficient number of OH groups on the surface of the catalyst for chemisorption to proceed. By comparing the effective cross-sectional areas of a molecule of isopropyl alcohol (40 A) and of an OH group (12 A), it can be concluded that even with the removal of 60% of the OH surface groups, which are surrounded by a close-packed monolayer of catalyst particles, chemisorbed isopropyl alcohol can cover the entire surface, since the cross section of an alcohol molecule is three times greater than the cross section of an OH group. A value of 13 μequiv/sq.m is given in the literature [7] for saturation of the surface of crystalline quartz or silica by OH groups. In only one of our samples was this value exceeded. In the remaining cases, the calculated values were less than 13 μequiv./sq. m; therefore, for the majority of the samples, the surface was characterized not only by the presence of hydroxyl groups, but also by the presence of oxygen atoms, which were joined to the metal as



LITERATURE CITED

[1] O. M. Dzhigit, N. N. Mikos-Avgul', A. V. Kiselev and K. D. Shcherbakova, Proc. Acad. Sci. USSR, 70, 441 (1950).

[2] K. V. Topchieva and A. P. Ballod, Proc. Acad. Sci. USSR, 75, 247 (1950).

[3] A. N. Terenin and N. G. Iaroslavskii, Proc. Acad. Sci. USSR, 66, 885 (1949).

[4] A. N. Terenin, Coll., Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, p. 206.

[5] A. A. Babushkin, L. A. Ignat'eva and N. N. Grigor'ev, Ibid, p. 246.

[6] A. A. Babushkin and A. V. Uvarov, Proc. Acad. Sci. USSR, 110, 581 (1956). **

*In Russian.

**Original Russian pagination. See C. B. Translation.

[7] A. V. Kiselev and G. G. Muttik, Coll. J., 19, 562 (1957).*

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INVESTIGATION OF THE CATALYTIC DEHYDROGENATION OF HYDROCARBONS AND ALCOHOLS OVER METALLIC RHENIUM

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In recent years, more and more attention has been given to the study and use of rhenium. In this connection, considerable significance attaches to the determination of its catalytic properties.

We have extended to rhenium the investigations of catalytic dehydrogenation which are being carried out in our laboratory (for a review of this work, see reference [1]). According to the multiplet theory of catalysis, selective dehydrogenation requires that the catalyst have an A1- or A3-type lattice and an atomic radius, r, in the range of 1.22-1.39 A [2]. It has subsequently become known that metallic rhenium has an A3 lattice and an atomic radius of 1.368 A. Thus, it fulfills the above conditions, and, consequently, the theory predicts that it should be a catalyst for the dehydrogenation of hydrocarbons with a six-membered ring. The structure and atomic radius of rhenium also satisfy the multiplet theory's principle of the retention of the valence angle [3,4]: therefore, rhenium could also be a catalyst for the dehydrogenation of hydrocarbons and alcohols by the duplet mechanism.

The catalytic properties of rhenium have not as yet been sufficiently studied experimentally. M. S. Platonov and co-workers[5] established that rhenium is an active catalyst for the dehydrogenation of alcohols, the process proceeding without side reactions, as a rule. Rhenium is not less active than copper. However, Platonov's optimum temperature for dehydrogenation over rhenium (400-450°) lies 100-150° higher than for copper [6], Fe, Co, and Ni [7]. Platonov was the first to discover that rhenium is capable of catalyzing the dehydrogenation of cyclohexane [8], thereby confirming the prediction of the multiplet theory. However, the experimental details and the method of catalyst preparation are still unknown. Therefore, it was necessary to carry out a more detailed investigation.

In the present work it was shown that rhenium supported on carbon is an active catalyst for the dehydrogenation of cyclohexane, its homologs, and cumene and for the dehydrocyclization of n-heptane. Dehydrogenation of alcohols in the temperature interval of 120-300° and conversion of 1,4-butanediol γ-butyrolactone also proceed over the catalysts prepared by us.

EXPERIMENTAL

Catalysts. Rhenium catalysts were prepared by a method developed as a result of a special investigation, in which different methods of preparation and different carriers were studied. The rhenium was deposited on activated carbon either as ammonium perrhenate (from aqueous solution) or as a complex of rhenium heptoxide with dioxane, $Re_2O_7 \cdot xC_4H_8O_2$ [9] (from solution in absolute methanol). The carbon, after impregnation with one solution or the other, was charged to the catalyst tube, and treated with hycrogen while the temperature was slowly raised to 500°. The reduction was carried out over a period of 4-5 hours. It was established that the most active catalyst is one which contains about 30 wt. % Re.

The materials which were passed over the catalyst had constants corresponding to the literature values.

TABLE 1

Dehydrogenation of Cyclohexane. Re–C. Catalyst volume, 10 ml. Feed rate, 0.2 ml/minute. Activation energy, E = 7.8 kcal./mole; average $k_0 = 1.7 \cdot 10^4$.

Temp. °C	m*	m, calc.	Anal. of gas, vol. %		$\frac{E}{\lg k_0}$
			H_2	CH_4	
246	0,98	0,90	88,6	11,4	2,40
272	1,35	1,29	90,0	10,0	2,40
281	1,49	1,45	88,0	12,0	2,41
284	1,50	1,48	88,2	11,8	2,46
341	2,70	2,82	86,4	13,6	2,44

* m – amount of gas in ml at STP produced per minute per ml of catalyst.

TABLE 2

Dehydrogenation of Methylcyclohexane. Re–C. Catalyst volume, 10 ml. Feed rate, 0.2 ml/minute: E = 10.3 kcal./mole; average $k_0 = 8.7 \cdot 10^3$.

Temp °C	m	Anal. of gas, vol. %		$\frac{E}{\lg k_0}$
		H_2	CH_4	
267	0,59	92,4	7,6	2,62
285	0,81	88,4	11,6	2,61
302	1,08	84,2	15,8	2,61
316	1,31	52,5	17,5	2,61

TABLE 3

Dehydrogenation of Ethylcyclohexane. Re–C. Catalyst volume, 10 ml. Feed rate, 0.1 ml/minute; E = 12.6 kcal./mole; average $k_0 = 3.5 \cdot 10^4$

Temp. °C	m	Anal. of gas, vol. %		$\frac{E}{\lg k_0}$
		H_2	CH_4	
286	0,39	91,3	8,7	2,78
322	0,80	90,0	10,0	2,77
399	1,11	86,0	14,0	2,77
388	2,23	77,7	2,23	2,79

Dehydrogenation of hydrocarbons. The catalyst prepared from NH_4ReO_4 proved to be less stable and less active than the catalyst prepared by the dioxane method during the dehydrogenation of cyclohexane. The first catalyst dehydrogenated cyclohexane at 350-450° with an activation energy of 12.8 kcal./mole, the catalyzate containing 1-1.5% cyclohexene in addition to benzene; the second dehydrogenated cyclohexane in the temperature interval 250-350° with an activation energy of 7.8 kcal./mole, and the catalyzate did not contain cyclohexene. We carried out the dehydrogenation of methylcyclohexane and ethylcyclohexane over the catalyst prepared by the dioxane route. As shown in Tables 1-3, the rate of dehydrogenation of hydrocarbons decreases and the activation energy increases with an increase in the molecular weight of the hydrocarbon; the difference in activation energy between adjacent members of the homologous series was about 2.5 kcal./mole.

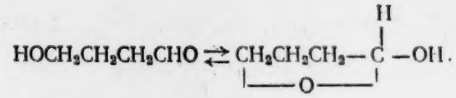
The hydrocarbon dehydrogenation process over both catalysts was accompanied by cracking of the hexamethylene ring, as indicated by the presence of methane in the gaseous reaction products.

The dehydrogenation of alcohols was studied with the catalyst prepared with the dioxane complex. The dehydrogenation of secondary alcohols (isopropyl and sec.-butyl) proceeded with practically no side reactions, if one does not count the small amount of decomposition of the resulting ketone which gave rise to small amounts of saturated hydrocarbons (1-8%) in the gas. The conversion of isopropyl alcohol to acetone at temperatures of 150-200° proceeds with yields close to the thermodynamic ceiling. The activation energies of the dehydrogenation of isopropyl and sec.-butyl alcohols are, respectively, 4.8 and 6.5 kcal./mole. The dehydrogenation of primary alcohols, ethyl, n-propyl, and n-butyl, proceeded somewhat more difficultly. The process was complicated by the formation of the ester and by the decomposition of the aldehyde formed. The activation energies for ethyl, n-propyl, and n-butyl alcohols were, respectively, 7.8, 9.5, and 11.7 kcal./mole.

From the data obtained, it is seen that the rate of dehydrogenation of an alcohol and the activation energy depend on the structure of the alcohol. The activation energy decreases by approximately 5 kcal./mole in the transition from a primary to the isomeric secondary alcohol. Moreover, with an increase in the molecular weight of the alcohol, the rate of the process decreases somewhat, and the activation energy increases, the difference between adjacent members of the homologous series being approximately 2 kcal./mole.

The dehydrogenation of 1,4-butanediol leads to the formation of γ-butyrolactone and γ-hydroxybutyraldehyde. We were unable to detect cinnamaldehyde in the catalyzate. The experimental results are presented in Table 4. The

activation energy of the process forming γ-butyrolactone was 11.5 kcal./mole, which corresponds to the activation energy for n-butyl alcohol. This provides a basis for the assumption that the limiting stage of the process is the splitting of one molecule of hydrogen from 1,4-butanediol with the formation of γ-hydroxybutyraldehyde. Moreover, it is known that hydroxyaldehydes exist in equilibrium with the tautomeric cyclic hemiacetal forms [10]:



The dehydrogenation of such a cyclic form should proceed very readily and lead directly to butyrolactone.

TABLE 4

Dehydrogenation of 1,4-Butanediol. Re–C. Catalyst Volume, 10 ml. Feed Rate 0.1 ml/minute.

Temp. °C	Amt. of gas, ml/min	Anal. of gas, vol. %					Catalyzate, wt. %	
		H_2	CO_2	CO	Unsaturates	CH_4	Butyrolactone	Hydroxyaldehyde
233	9,99	100	—	—	—	—	11,9	16,5
252	11,60	—	—	—	—	—	16,8	14,9
261	16,20	91,0	0,8	2,4	2,9	2,9	22,5	15,4
297	22,87	92	1,4	1,8	2,2	2,6	36,2	14,1
306	24,61	85,7	—	2,8	3,2	8,3	46,3	10,3

With the aim of confirming this assumption, we synthesized γ-hydroxybutyraldehyde [12] and cinnamaldehyde [13], and studied their conversion over rhenium catalyst. It was found that γ-hydroxybutyraldehyde is readily converted to γ-butyrolactone, and the percent conversion, which is 40-48%, depends little on temperature in the interval 230-300°, which indicates a low activation energy for this process. Cinnamaldehyde was not detected in the products of the conversion. Cinnamaldehyde did not give butyrolactone when passed over rhenium catalyst. The major portion of it was unchanged, and a part was converted into condensation products. Reppe prepared the commercially important γ-butyrolactone by dehydrogenation of 1,4-butanediol over Cu [13], and he considered that the reaction proceeded through cinnamaldehyde. In contradiction to this proposal of Reppe, it was shown in our work that the intermediate product of the conversion of 1,4-butanediol to γ-butyrolactone is γ-hydroxybutyraldehyde, and not cinnamaldehyde, the formation of the first being the limiting stage of the process.

LITERATURE CITED

[1] A. A. Balandin, J. Phys. Chem., 31, 745 (1957).

[2] A. A. Balandin, J. Russ. Phys.-Chem. Soc., Chem. Sec. 61, 909 (1929).

[3] A. A. Balandin and Ia. T. Eidus, Proc. Acad. Sci. USSR, 49, 15 (1946).

[4] A. A. Balandin, Sci. Reports Moscow State Univ., 175, 97 (1956).

[5] M. S. Platonov and coworkers, J. Gen. Chem., 5, 1059 (1935); 6, 855 (1956); 7, 776, 778, 1361, 1803, 2895 (1937); 11, 590 (1941).

[6] A. A. Balandin and P. Teteni, Proc. Acad. Sci. USSR, 113, 1090 (1957).*

[7] A. A. Balandin and P. Teteni, Proc. Acad. Sci. USSR, 115, 727 (1957).*

*Original Russian pagination. See C. B. translation.

[8] M. S. Platonov, Abstracts of Reports at the Conference on Heterogeneous Catalysis, Moscow, 1940, p. 35. *

[9] Inorganic Syntheses, Coll. Vol. 3, Foreign Lit. Press, 1952, p. 174. (Russian Translation).

[10] C. D. Hurd, W. H. Saunders, J. Am. Chem. Soc., 74, 5324 (1952).

[11] R. Paul, S. Tchelitcheff, Bull. Soc. Chim. France, 197 (1948).

[12] J. Fakstorp, D. Raleigh, L. E. Schniepp, J. Am. Chem. Soc., 72, 869 (1950).

[13] W. Reppe, Chem. Ing. Tech., 22, 361, 437, 527 (1950).

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CONTRIBUTION TO THE PROBLEM OF THE EFFECT OF PRESSURE ON THE RATE OF STERICALLY HINDERED REACTIONS

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(Presented by Academician B. A. Kazanskii, April 29, 1958)

The few available experimental data indicate a significant acceleration of sterically hindered reactions with an increase in pressure. Thus, tetramethylethylene is completely polymerized in 3 hours at 23,000 atmospheres and 300°, while it is polymerized to the extent of only 20% after 50 hours at this same temperature and a pressure of 200 atmospheres [1]. Pressure also considerably accelerates the thermal conversion of tetrachloroethylene to hexachlorobutadiene and hexachloroethane at 300° [2]. In both of these cases, the observed acceleration of the reactions by pressure is connected in only a slight degree with the increase in the concentrations of the initial materials; the determining factor here is the increase in the reaction rate constants with an increase in pressure.

According to transition state theory, the change in the reaction rate constant with pressure is determined by the magnitude of the change in volume during the formation of the activated complex ($\Delta v^{\neq}$) [3]:

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta v^{\neq}}{RT}. \tag{1}$$

It is evident that an important component of the value of $\Delta v^{\neq}$ is the change in the volume of both of the reacting molecules during the formation of the activated complex($\Delta v^{\neq}_{mol}$); in addition to this, other volume effects play important roles, particularly the change in the volume of the solvent (if the reaction is carried out in solution) as the result of a difference in the degree of solvation of the reacting molecules and that of the activated complex ($\Delta v^{\neq}_{solv}$). In the present work, we shall consider only the value $\Delta v^{\neq}_{mol}$. Moreover, we shall limit our considerations to Menshutkin reactions, for which it is possible, with reasonable assurance, to make use of a specific geometric model of the transition state. Moreover, it should be remarked that Menshutkin reactions have served as subjects of a series of kinetic investigations at high pressures.

Neglecting the possible participation of the solvent in Menshutkin reactions [4], we shall start from the representations of the structure of the activated complex shown schematically in Fig. 1 [5]. According to this scheme, the C–R', C–R", and C–R'''bonds lie in the same plane. As regards the N–C (or N–H) bonds in the amines, their disposition relative to the plane passing through the nitrogen atom and parallel to the CR_3 plane depends on the structure of the amine molecule. Thus, if in the amine the nitrogen is bonded to alkyl radicals or hydrogen atoms, then these bonds are disposed pyramidally (with angles between them of 108°). If the radical is a phenyl radical, then the N–C bond in the amine molecule lies in a plane which, according to our assumption, is parallel to the CR_3 plane. Finally, for the complex with pyridine it is most probable that the pyridine ring is disposed perpendicularly to the CR_3 plane.

The N...C distance in the activated complex is taken as equal to an N–C valence bond (1.5 A), although the possibility is not excluded that it is actually somewhat greater (see reference [6]). The mutual approach of the N and C atoms to such a distance does not, of itself, guarantee the decrease of 8.4 A^3 in the volume of the activated complex in comparison with the volumes of the reacting molecules, i.e., a decrease of 5 cc/mole for all Menshutkin reactions.*

* Here and throughout this paper, we shall use the following values of molecular radii for calculations of the compression during the formation of the activated complex [7]: R_H = 1.2 A; R_N = 1.6 A; R_C = 1.8 A; R_{CH_3} = 2.0 A. The lengths of the C–H and C–C bonds are taken as 1.1 and 1.55 A, respectively.

However, along with this volume effect during the formation of the activated complex, additional compressions arise, since the mutual approach of the two planes shown in Fig. 1 to a distance of 1.5 A leads to the circumstance that the distances between certain atoms not bonded by valence bonds become less than the sums of their intermolecular radii (we assume that the new bond formed during the reaction, an N–C bond in our case, is a valence bond).

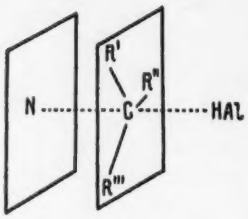


Fig. 1. Scheme of the structure of the activated complex in Menshutkin reactions.

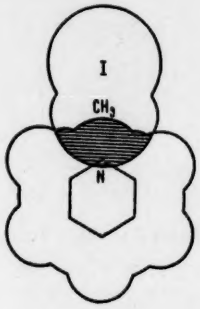


Fig. 2. The activated complex in the reaction of pyridine with methyl iodide. The compression is crosshatched.

These additional compressions characterize (though certainly not completely) the steric retardation of the reactions. From such considerations it appears that Menshutkin reactions are sterically hindered.

The reaction with pyridine. In the pyridine molecule, only one nitrogen atom lies in the plane parallel to the CR'R"R''' plane and perpendicular to the nucleus (Fig. 2). The two ortho-hydrogens fail to reach this plane (by ~0.2 A), and the two ortho-carbons fail by 0.7 A. During the reaction with methyl iodide, compression arises between the nitrogen atom and the three hydrogen atoms (1.85 A), between one hydrogen atom in CH_3I and an H atom in the C_5H_5N (1.7 A in place of 2.4 A), and also between the C atoms in the C_5H_5N and the H atoms in the CH_3I. The total of these compressions is 6.7 A^3, i.e., 4 cc/mole; $\Delta v^{\neq}_{mol} = -9$ cc/moles. *

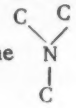
In the reaction with ethyl iodide, one N...H compression is replaced by an N...CH_3 (2.15 A in place of 3.6 A), and the interactions with the ortho-carbons is increased; $\Delta v^{\neq}_{mol} = -14$ cc/mole.

The value of $\Delta v^{\neq}_{mol}$ does not change with a further increase in the number of carbon atoms in the normal chain of the alkyl halide.

In the reaction with isopropyl iodide, there are two N...CH_3 compressions, and the nature of the interaction with the ortho-carbons changes somewhat; $\Delta v^{\neq}_{mol} = -19$ cc/mole.

Reactions with trimethylamine. We shall consider the reaction of trimethylamine with isopropyl iodide. The most preferred disposition of the CH_3 plane and the $N(CH_3)_3$ pyramid is shown in the scheme of Figure 3a (view along the C–I bond).

The following compressions arise in the activated complex: an N...H compression (1.85 A), two N...CH_3 compressions (2.15 A), two CH_3...H compressions (2.6 A), and four CH_3...CH_3 compressions (2.7 A). The calculated value of $\Delta v^{\neq}_{mol}$ is -24 cc/mole, which is greater than for the reaction of isopropyl iodide with pyridine. This value does not change upon substitution of triethylamine for trimethylamine.

Reactions with dimethylaniline. In a free molecule of dimethylaniline, the plane of the phenyl radical stands out from the  plane owing to steric interactions of the two ortho-hydrogens with the methyl groups. During

* Taking into consideration also the formation of the C–N bond (see above).

the formation of the activated complex, the phenyl radical turns so that all carbon atoms fall in a single plane. This rotation is accompanied by the emergence of two compressed distances (inside the molecule); these are two CH_3...H of 2.5 A, which lead to an insignificant compression of the volume.

The mutual disposition of the approaching planes during the reaction of dimethylaniline with isopropyl iodide is shown in Figure 3b (view from the side of the I atom). The following compressions arise in the activated complex: one N...H (1.85 A), two N...CH_3 (2.15 A), one H...H (2.1 A), two H...C (1.9 and 2.1 A), two CH_3...H (1.8 and 2.0 A), two CH_3...C (2.0 and 2.1 A), and three CH_3...CH_3 (2.1 A). The value of $\Delta v^{\neq}_{mol}$ for this reaction is −44 cc/mole.

In the reactions of dimethylaniline with methyl iodide and ethyl iodide, the value of $\Delta v^{\neq}_{mol}$ is, respectively, −19 and −29 cc/mole.

Substitution of the ortho-hydrogen in the dimethylaniline molecule by a methyl group leads to some decrease in $(-\Delta v^{\neq}_{mol})$ for the reaction with methyl iodide (to 22 cc/mole).

Thus, the values of $(-\Delta v^{\neq}_{mol})$ calculated according to the scheme presented above, attain, for certain Menshutkin reactions, values of several tens of cubic centimeters per mole, which, according to Equation (1), must lead to a very significant acceleration of these reactions with an increase in pressure. Such an acceleration actually takes place, as may be seen from the data presented in the Table. For the Menshutkin reactions investigated, the ratio of the rate constant at a pressure of 3000 kg/sq. cm to that at atmospheric pressure (K_{3000}/K_1), which characterizes the acceleration of the reaction with an increase in pressure, changes in parallel with the calculated values of $(-\Delta v^{\neq}_{mol})$ for the reactions considered.

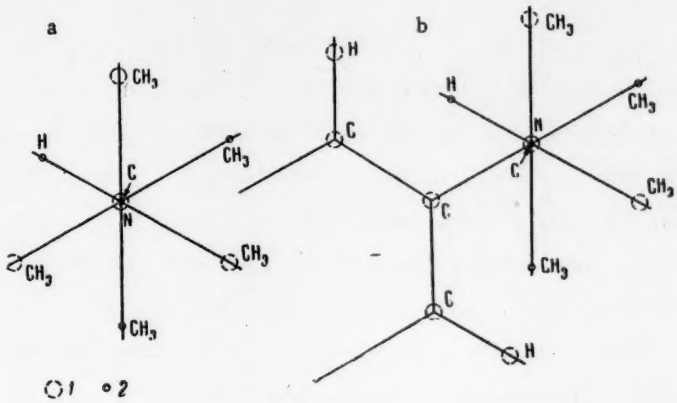


Fig. 3. Diagram of the structure of the activated complex (view along the C–I bond) in the reactions: a) trimethylamine + isopropyl iodide, b) dimethylaniline + isopropyl iodide; 1) centers of amine atoms, 2) centers of alkyl halide atoms.

Thus, calculation of the steric retardation of the process of activated complex formation (defined by us as the mutual approach of atoms not bonded by valence bonds to a distance less than the sum of their intermolecular radii) permits a qualitative explanation of the different acceleration by pressure of Menshutkin reactions differing in the structure of the participating amines and alkyl halides. In particular, it becomes understandable why there is an increase in the acceleration of these reactions by pressure on changing from CH_3I to C_2H_5I and iso-C_3H_7I* and from C_5H_5N to $(CH_3)_3N$ and $C_6H_5N(CH_3)_2$, as well as the uniform effect on reactions of trimethylamine and triethylamine. Naturally, for a complete analysis of the effect of pressure on the rate of Menshutkin reactions, it is necessary to take into consideration all of the components of $\Delta v^{\neq}$.

*Supplemental to the data in Table 1, we point out that in reactions of dimethylaniline with CH_3I and C_2H_5I in methanol at 25°, the values of K_{3000}/K_1 are, respectively, 10 and 12 [11].

TABLE

Values of $\Delta v^{\neq}_{mol}$ and the Effect of Pressure on the Rate Constant of Menshutkin Reactions (in acetone at 60°)

Reaction	$\Delta v^{\neq}_{mol}$ cc/ mole	K_{3000}/K_1
$C_5H_5N + CH_3I$	−9	6.8 [8]
$C_5H_5N + C_2H_5I$	−14	7.9 [9]
C_5H_5N + n. C_4H_9I	−14	6.5 [8]
C_5H_5N + iso-C_3H_7I	−19	9.6 [8]
o-CH $C_6H_4N(CH_3)_2 + CH_3I$	−22	11.5 [10]
$(CH_3)_3N$ + iso-C_3H_7I	−24	16.4 [8]
$(C_2H_5)_3N$ + iso-C_3H_7I	−24	16.0 [8]
$C_6H_5N(CH_3)_2$ + iso-C_3H_7I	−44	25.5 [8]

We believe that the concepts developed in this work and the simple calculations which were carried out, in spite of their approximate nature, permit an explanation of the significant acceleration of sterically hindered reactions with an increase in pressure. In addition, it may be pressumed that the study of the kinetics of reactions at elevated pressures is useful for confirming these or other concepts of the structure of the activated complex in these reactions.

LITERATURE CITED

[1] M. G. Gonikberg, V. P. Butuzov and V. M. Zhulin, Proc. Acad. Sci. USSR, 97, 1023 (1954).

[2] M. G. Gonikberg and V. M. Zhulin, Bull. Acad. Sci. USSR; Div. Chem. Sci., 1957, 510.*

[3] M. Evans, M. Polanyi, Trans. Farad. Soc., 21, 875 (1935).

[4] C. G. Swain, R. W. Eddy, J. Am. Chem. Soc., 70, 2989 (1948).

[5] C. K. Ingold, Structure and Mechanism in Organic Chemistry, N. Y., 1953, p. 403.

[6] C. K. Ingold, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1956, 1016.*

[7] A. I. Kitaigorodskii, Organic Crystallochemistry**, Acad. Sci. USSR Press, 1955, p. 15.

[8] M. W. Perrin, E. G. Williams, Proc. Roy. Soc., A, 159, 162 (1937).

[9] R. O. Gibson, E. W. Fawcett, M. W. Perrin, Proc. Roy. Soc., A, 150, 223 (1935).

[10] K. E. Weale, Disc. Farad. Soc., No. 22, 122 (1956).

[11] S. D. Hamann, D. R. Teplitzky, Disc. Farad. Soc., No. 22, 114 (1956).

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THE MOBILITY OF RS GROUPS IN ORGANIC THIOSULFONATES (SULFONESULFIDES)

N. I. Grishko and E. N. Gur'ianova

(Presented by Academician I. L. Knuniants, April 28, 1958)

Over a period of several years, discussions concerning the structure of "disulfoxides" have appeared in the literature:

$$R-SO-SO-R' \quad (I) \quad \text{or} \quad R-SO_2-S-R' \quad (II)$$

Chiefly on the basis of preparation reactions, it was first assumed that these compounds have the disulfoxide structure (I); they entered into the chemical literature under sulfoxide names. Recently, in connection with the discovery [1, 2] of the antibacterial and antibiotic properties of these substances, interest in them has increased considerably, and many new compounds of this class have been synthesized [3]; this has lead to the appearance of more and more data – both purely chemical and physicochemical – in support of the sulfone sulfide [thiosulfonate] structure (II).

We have previously measured the dipole monents and obtained the vibrational spectra of a large group of thiosulfonate esters [4], and we also conclude that the sulfonesulfide structure (II) of "disulfoxides" is correct.

TABLE 1

System	Temp. °C	Time, hours	Activity, imp./min. before exchange: ester	before exchange: disulfide	after exchange: ester	after exchange: disulfide	at equilibrium (calc.): ester	at equilibrium (calc.): disulfide	% exchange
$C_3H_5SO_2-\overset{*}{S}C_3H_5+$ $+C_3H_5S-SC_3H_5$	20	2	4050	0	—	1834	1350	2700	67
$C_6H_5SO_2-SC_6H_5+$ $+C_6H_5\overset{*}{S}-\overset{*}{S}C_6H_5$	23	2	0	640	0	643	213	426	0
Same	61	0,5	0	120	40	84	40	80	100
	65	0,25	0	640	206	410	213	426	100
$C_2H_5\overset{*}{S}O_2-SC_2H_5+$ $+C_2H_5\overset{*}{S}-\overset{*}{S}C_2H_5$	25	5	0	1386	0	1380	462	924	0
Same	100	5	0	1386	0	1382	462	924	0
" "	162	1	0	2676	260	2150	892	1784	~30
" "	170	3	0	1386	469	915	462	924	100

In the present work, the method of tagged atoms was used to study the questions of the structure and reactivity of these compounds; up to the present, this method has not been applied to the investigation of this interesting and important class of substances. We hoped to obtain, with the aid of this method, additional information on the structure of thiosulfonate esters as well as their reactivity with other sulfur-containing substances. A study of the mechanism of the interaction of thiosulfonate esters with model compounds containing sulfhydryl [mercapto] and disulfide groups could not only yield information on the effect of structure on reactivity, which is of general

theoretical interest, but could also shed light on the mechanism of the antibacterial action of these compounds.

As would be expected, an attempt to carry out isotope exchange of sulfur between thiosulfonate esters and radioactive elemental sulfur was unsuccessful. Not one of the compounds investigated – the ethyl ester of toluenethiosulfonic acid, the tolyl ester of toluenethiosulfonic acid, the ethyl ester of ethanethiosulfonic acid, and the phenyl ester of benzenethiosulfonic acid – exchanged with radioactive elemental sulfur when heated to 170°. Considering the results of the work reported in reference [5] on the exchange of RS groups between organic polysulfides and also between disulfides and mercaptans, it would be expected that, if the compounds investigated have the sulfonesulfide configuration (II) and not the disulfonoxide structure (I), they would exchange RS groups with the corresponding disulfides under certain conditions.

The results of experiments on the exchange of sulfur between thiosulfonate esters and disulfides are presented in Table 1; in all cases, the activity of benzidine sulfate precipitates was determined. As may be seen from the data in Table 1, isotope exchange of sulfur was observed in all of the systems investigated under the specific conditions used. For proof that the radioactive isotope of sulfur was shifted from one molecule to the other by an exchange of RS groups rather than by an exchange of sulfur atoms, experiments were carried out in which the exchange was between thiosulfonate esters and disulfides with different R groups. Equimolar amounts of the tolyl ester of toluenethiosulfonic acid and labeled diethyl disulfide were held for 3.5 hours at 162°. If an exchange of groups takes place, the reaction mixture should contain the labeled ethyl ester of toluenethiosulfonic acid:

$$CH_3C_6H_4SO_2SC_6H_4CH_3 + C_2H_5\overset{*}{S} - \overset{*}{S}C_2H_5 \rightarrow CH_3C_6H_4SO_2 - \overset{*}{S}C_2H_5 + CH_3C_6H_4S - \overset{*}{S}C_2H_5$$

The ethyl ester of toluenethiosulfonic acid was isolated by vacuum fractionation and was identified: b.p. 115°/4 mm, $n^{20}D = 1.5731$, sulfur found 29.3%, sulfur calculated 29.6%. The radioactivity of the sulfur in the thio ester group matched the activity of the original diethyl disulfide (3242 and 3260 imp / minute, respectively). Consequently, the radioactive sulfur isotope is transferred from the disulfide molecule to the thio ester molecule together with an ethyl radical; i.e., an exchange of RS groups occurs. That an exchange of RS groups occurs in the systems investigated is a very weighty argument in support of the sulfonesulfide structure (II) of thiosulfonate esters.

We propose that now, as a result of the entire accumulation of investigations, the thiosulfonate or sulfonesulfide structure (II) of "disulfoxides" can be considered proved.

From the data in Table 1, it is seen that the exchangeability of RS groups between thiosulfonate esters and disulfides depends to a considerable extent on the nature of the R radicals. The allyl ester of allylthiosulfonic acid (pseudoallicin) exchanged C_3H_5S groups with allyl disulfide even at room temperature; similar compounds with phenyl radicals exchanged C_6H_5S groups when heated slightly (50-60°); while the derivatives with ethyl radicals exchanged only at ~ 160°.

In order to clarify the extent to which the R and R' groups affect the exchangeability of RS groups in the systems investigated, the rate of isotope exchange of sulfur was measured between the ethyl esters of certain thiosulfonic acids, on the one hand, and labeled diethyl disulfide, on the other. The rate constants, K, for isotope exchange at a temperature of 162° are presented below:

Ethyl Ester	$K \cdot 10^3$, sec.$^{-1}$
Ethanethiosulfonic acid $C_2H_5SO_2$–SC_2H_5	0.25
Benzenethiosulfonic acid C_6H_5–SO_2–SC_2H_5	0.14
β-Naphthalenethiosulfonic acid $C_{10}H_7SO_2$–SC_2H_5	0.41
p-Bromobenzenethiosulfonic acid $BrC_6H_4SO_2$–SC_2H_5	0.32
p-Toluenethiosulfonic acid $CH_3C_6H_4SO_2$–SC_2H_5	0.44
p-Nitrobenzenethiosulfonic acid $NO_2C_6H_4SO_2$–SC_2H_5	1.05

The ethyl esters of the various thiosulfonic acids exchanged C_2H_5S groups with labeled diethyl disulfide under approximately the same conditions; exchange proceeded at a measureable rate at 162°. All of the observed deviations in the isotope exchange rate constants fall within an order of magnitude.

From a comparison of these data and those presented in Table 1, it can be concluded that the composition

and structure of the R' radical in the thiol R'S group exerts a considerably greater effect on the reactivity of the system $RSO_2 - SR' + R'S-SR'$ than does the R radical joined to the sulfone group. It should be remarked that this result, which we obtained through a study of the mobility of RS groups in model systems, is in agreement with the data of Belous [6] and of Boldyrev [7] obtained in studies of the antibacterial properties of various esters of thiosulfonic acids. For example, it was shown [6] that replacement of the allyl group adjacent to the sulfonyl group by a phenyl group, allyl—SO_2—S—allyl and phenyl—SO_2—S—allyl, caused practically no change in the antibacterial activity, while a similar replacement of the allyl radical in the R'S group by a phenyl group gave a compound which was only slightly active. However, the data on the effect of radicals on the reactivity of thiosulfonate esters are still far from sufficient for the drawing of deeper conclusions.

The occurrence of the exchange of RS groups between thiosulfonate esters and disulfides observed in the present work is very interesting, especially in connection with the antibacterial activity of the thiosulfonate esters.

The question of the mechanism of the antibacterial action of these compounds has appeared in the literature; however, the answer is still far from clear. Some authors [1,2], basing their thoughts on reactions of thiosulfonate esters with mercaptans and with compounds containing mercapto groups (cysteine, glutathione), have proposed that the mechanism of the antibacterial action consists of a blocking of the mercapto groups of the metabolite according to the reaction:

$$R - SO_2 - SR' + R''SH \rightarrow RSO_2H + R''S - SR'$$

As a result of this, there is a disruption of the exchange processes of the bacterial cells.

The results of the present work indicate that the thiosulfonate esters can react not only with the mercapto groups, but also with the disulfide groups of compounds and, presumably, with the disulfide bonds of albumin molecules. Therefore, the mechanism of the antibacterial action of thiosulfonate esters can be other than that proposed earlier.

We believe that it is necessary to take into consideration possible reactions with the disulfide groups of albumin during investigation of the antibacterial and antibiotic activity of thiosulfonate esters.

LITERATURE CITED

[1] M. A. Belous and I. Ia. Postovskii, J. Gen. Chem., 20, 1701 (1950). *

[2] L. D. Small, J. H. Bailew, C. J. Cavallitto J. Am. Chem. Soc., 71, 3565 (1949).

[3] B. G. Boldyrev, Sci. Records L'vov Polytech. Inst., No. 22, 71 (1956).

[4] N. I. Grishko and E. N. Gur'ianova, J. Phys. Chem. (in press).

[5] E. N. Gur'ianova, Ia. K. Syrkin and L. S. Kuzina, Proc. Acad. Sci. USSR, 86, 107 (1951); E. N. Gur'ianova and V. N. Vasil'eva, J. Phys. Chem., 28, 160 (1954).

[6] M. A. Belous, Synthesis and Structure of New Antibacterial Substances of the Sulfone Series.** Dissertation, Sverdlovsk, 1947.

[7] B. G. Boldyrev and T. A. Trofimova, J. Gen. Chem., 27, 1006 (1957). *

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THE STRUCTURE OF POLYNUCLEAR DOUBLY CHARGED URANIUM-OXYGEN COMPLEXES AND THEIR DISPOSITION IN THE STRUCTURE OF THE AQUEOUS SOLUTION

I. I. Lipilina

(Presented by Academician I. I. Cherniaev, May 6, 1958)

In dilute solutions of uranyl salts, which are 2–1-electrolytes, the uranyl ion, UO_2^{2+}, has a coordination number of 6 and is located in the channels in the structure of the water along the axis of the channel [1]. Hydrolysis leads to the formation of polynuclear complexes in the solution [2-7]; the most accurate information may be considered to be that relating to the existence of the ions $U_2O_5^{2+}$ and $U_3O_8^{2+}$. As we visualize it, 2 (or 3) uranyl ions, each of which is surrounded by 6 molecules of water, are disposed in 2 (or 3) neighboring channels of one layer of the water structure (Figures 1a and 2a). It is in just this case that hydrolysis can proceed:

$$2UO_2^{2+} + H_2O \rightleftarrows U_2O_5^{2+} + 2H^+,$$
$$3UO_2^{2+} + 2H_2O \rightleftarrows U_3O_8^{2+} + 4H^+.$$

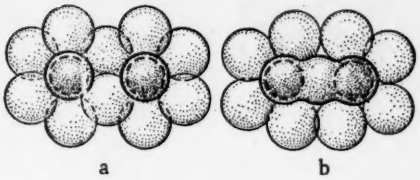


Fig. 1. Formation of the ion $U_2O_5^{2+}$: a) 2 uranyl ions in neighboring channels of the water structure; b) a $U_2O_5^{2+}$ ion, formed from 2 uranyl ions connected by a O^{2-}. ion. The O_I–U–O_I axis of the uranyl ion is perpendicular to the plane of the figure which coincides with the equatorial plane of the uranyls; one oxygen atom, O_I, is behind the plane of the figure, while the other is in front of it; the projection of the oxygen atoms onto the plane of the figure is shown by the broken lines; the water molecules are denoted by the light solid lines; the contour of the complex in the equatorial plane is denoted by the heavy solid line.

The charge on the uranyl ion is centered in the uranium atom, and the oxygen atoms are almost electrically neutral [8]; therefore, the U–O–U bond is formed in the equatorial plane, which is common to the reacting uranyl ions. Since the complex ions exist as independent entities, the U–O bond in them must be stable with a considerable degree of covalence. In clarifying the structure of these complexes, considerable significance is attached to the fact that they form not only during hydrolysis, but also during the solution of uranium trioxide in solutions of uranyl salts [2]. In both cases, the color of the solution changes from the yellow-green characteristic of aqueous solutions in which the uranyl ion is present to the orange color characteristic of uranium trioxide ; this indicates the formation in the solution of components in which there is the uranyl bond characteristic of uranium trioxide (the U–O distance is of the order of 2.0 A) [9,10]. With the above as a basis, we consider that $U_2O_5^{2+}$ and $U_3O_8^{2+}$ in solution have the structures represented in Figures 1b and 2b. The linear uranyl ion is positioned perpendicularly to the linear U–O–U–O... chain, which is disposed in one layer of the water structure; the U–O_I distance in the individual uranyls and in the U–O... chain is of the same order. The complexes contain elements of this same chain with the uranyl bond which occurs in UO_3, but there is an essential difference in that in $U_2O_5^{2+}$ and $U_3O_8^{2+}$ both a chain with a uranyl bond and individual UO_2^{2+} ions are present; i.e., the uranyl bond will occur in two mutually perpendicular directions. A non-linear structure of the polynuclear complex $U_3O_8^{2+}$ with the formation

of a $\begin{array}{c} U \\ / \quad \backslash \\ U\text{—}U \end{array}$ triangle in the equatorial plane common to the uranyls is, it seems to us, improbable, since each atom of uranium would have to form two unsymmetrically situated bonds in the equatorial plane. The complexes under consideration cannot have structures in the form of $[O_I\text{–}U\text{–}O_I]\text{–}O\text{–}[O_I\text{–}U\text{–}O_I]\text{–}\ldots$, chains, since a uranyl ion, as a consequence of its electrically neutral oxygens, does not form stable axial bonds.

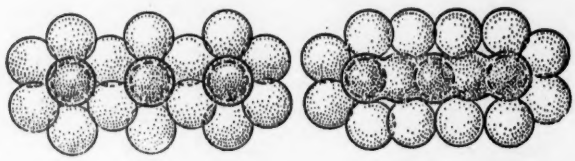
Owing to steric factors, 6 water molecules cannot now be located about a uranyl ion and enter the composition of the complex ion; however, each uranyl will be surrounded in the equatorial plane by water molecules in the manner most closely approximating the surrounding of a uranyl ion in solution. The $U_2O_5^{2+}$ ion will be surrounded in the equatorial plane by 8 water molecules, and the $U_3O_8^{2+}$ ion will be surrounded by 12 molecules, as shown in Figures 1b and 2b, which are drawn to scale. The coordination number of the end uranyls in polynuclear complexes decreases to 5, but inside the coordination number is 6 (in the equatorial plane, 4 water molecules and 2 oxygen atoms). The number of water molecules about a complex of n uranium atoms in 4n.

The general formula for the composition of doubly charged positive uranium–oxygen complexes constructed on the principle of a linear chain of uranyls disposed in neighboring channels of the water structure and connected by oxygen atoms is:

$$[U_nO_{3n-1}]^{2+}. \tag{1}$$

The formula can be written in a form showing that the complexes are constructed from uranyls:

$$[n\,UO_2^{2+} \cdot (n-1)\,O^{2-}]^{2+}. \tag{2}$$



a b

Fig. 2. Formation of the ion $U_3O_8^{2+}$: a) 3 uranyl ions in neighboring channels in the water structure; b) a $U_3O_8^{2+}$ ion formed from 3 uranyls joined in a linear chain by O^{2-} ions. The legend is the same as in Figure 1.

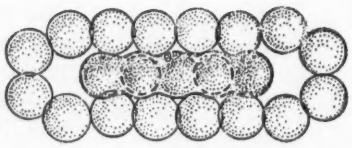


Fig. 3. Formation of the ion $U_2O_7^{2-}$: 2 uranyl ions located in neighboring channels in the water structure; and joined in a linear chain by an O^{2-} ion; O^{2-} ions are also found at both ends of the chain. The legend is the same as in Figure 1.

In these formulas, n is the number of uranium atoms or the number of uranyl ions. Both in Formula (1) and in Formula (2), when n = 1, we have the uranyl ion, UO_2^{2+}; when n = 2, we obtain the ion $U_2O_5^{2+}$; when n = 3, we obtain the ion $U_3O_8^{2+}$. The next ion will be $U_4O_{11}^{2+}$; it is possible that it is present in solution in some very small amount, but complexes with larger values of n have not been experimentally observed in solution. Ahrland, Hietanen and Sillen [6] proposed for polynuclear uranyl complexes in solution the formulas $UO_2 \cdot [(OH)_2UO_2]_n^{2+}$ and $UO_2(OUO_2)_n^{2+}$, which were obtained by mathematical treatment of data on the hydrolysis of the uranyl ion. Ahrland et al. solve the problem of the structure of polynuclear uranyl complexes by analogy with the structure of $Ba(UO_2)O_2$, $Ca(UO_2)O_2$ and $UO_2(OH)_2$ crystals without taking into account the structures of the water

and the aqueous solutions containing the uranyl ions. They assume that, with an increase in n, polynuclear uranyl complexes in aqueous solution form a planar layer in which there is the coordination UO_2–4O or UO_2–6OH. Our concept, presented above, of the linear structure of $U_2O_5^{2+}$ and $U_3O_8^{2+}$ with the coordination UO_2–2O, $4H_2O$ for uranyls located in the inner part of the chain and the coordination UO_2–O, $4H_2O$ for uranyls located at the ends of the chain differs from the structure of the complexes as proposed by the indicated authors, since, first, our concept emerges from the experimentally determined coordination number of uranyl in aqueous solution and the disposition of uranyl ions in channels in the structure of the water [1], and, second, from the presence in uranyl complexes of the U–O... chain with the uranyl bond characteristic of UO_3. The composition of positive polynuclear complexes can be described both by our formulas (1) and (2) and by the second formula of Ahrland et al.: the first formula of these authors is not in agreement with ours.

With an increase in the pH of solutions of uranyl salts, negative, not positive, polynuclear uranium-oxygen complexes are formed in the solution. Let us consider the following experimentally established compounds: uranate, Na_2UO_4, diuranate, Na_2UO_7, tetrauranate, CaU_4O_{13} [7], heptauranate, $Na_2U_7O_{22}$ [11], and octauranate, $Na_2U_8O_{25}$ [12]. There are complex anions in all of these cases. On the basis, first, that the presence of UO_2^{2+} in uranates has been established by x-ray methods [13, 14], and, second, that the formation of negative polynuclear complexes is merely the next step after the formation in the solution of positive polynuclear complexes [11], we believe that polynuclear uranium-oxygen anions should be considered as uranyl-oxygen complexes. The uranyl groups are disposed in channels in the structure of the water in a manner such that their equatorial planes coincide, and the uranium and oxygen atoms in this plane are located on a straight line, forming the very same chain with the uranyl bond, O–U–O... which is found in positive complexes; however, there are oxygen atoms at the end of the chain in negative complexes (Figure 3), which differentiates these complexes from the positive complexes, in which there are uranium atoms at the ends of the chain.

The following general formula can be proposed for polynuclear uranium-oxygen complexes bearing the charge (–2):

$$[U_nO_{3n+1}]^{2-}.$$

When n = 1, the ion is UO_4^{2-}; when n = 2, $U_2O_7^{2-}$; when n = 4, $U_4O_{13}^{2-}$; when n = 7, $U_7O_{22}^{2-}$; when n = 8, $U_8O_{25}^{2-}$. We are not disregarding that, depending on the pH of the solution, other polynuclear complexes can exist in solution, for examples, at n = 3, the complex $U_3O_{10}^{2-}$. Just as in the case of the positive complexes, the general formula expressing the composition of negative polynuclear complexes can be written in a form which emphasizes the presence of uranyl

$$[n\,UO_2^{2+} \cdot (n+1)\,O^{2-}]^{2-}.$$

If we compare the formulas for the positive and negative complexes, it is impossible not to see their very close resemblance, since they reflect in principle the uniform structure of doubly charged cations and anions (a linear chain of uranyls joined by oxygen atoms); the difference in the structures of these complexes is the presence of oxygen atoms at the ends of the chain of a negative complex and the presence of uranium atoms at the ends of the chain of a positive complex.

Hexavalent uranium can form various uranium-oxygen configurations with the uranyl bond in mutually perpendicular directions. When the uranyl bond is in one direction, linear configurations are formed (uranyl ion; the chain with uranyl bonds in α-UO_3). The polynuclear complexes considered here provide examples of the more complex uranium-oxygen configurations where the uranyl bond is in two mutually perpendicular directions. We consider the cubic modification of UO_3 [15] and of $UO_2(OH)_2$ [16] to be compounds in which the uranyl bond is observed in 3 mutually perpendicular directions in space.

LITERATURE CITED

[1] I. I. Lipilina and O. Ia. Samoilov, Proc. Acad. Sci. USSR, 98, 99 (1954).

[2] J. Sutton, J. Chem. Soc., Suppl. Iss., No. 2, 275 (1949).

[3] J. Faucherre, C. r, 227, 1367 (1948).

[4] J. Faucherre, Bull. Soc. Chim. France, No. 2, 253 (1954).

[5] S. Ahrland, Acta Chem. Scand., 3, 374 (1949).

[6] S. Ahrland, S. Hietanen, L. G. Sillen, Acta. Chem. Scand., 8, 1907 (1954).

[7] T. V. Arden, J. Chem. Soc., Suppl. Iss., No. 2, 299 (1949).

[8] J. L. Hoard, J. D. Stroupe, in the book by G. H. Diecke, A. B. F. Duncan, Spectroscopic Properties of Uranium Compounds, N. Y., 1949.

[9] W. H. Zachariasen, Acta. Cryst., 1, 265 (1948).

[10] N. V. Belov, Proc. Acad. Sci. USSR, 65, 677 (1949).

[11] C. A. Wamser, J. Belle, E. Bernsohn, B. Williamson, J. Am. Chem. Soc., 74, 1020 (1952).

[12] H. Guiter, Bull. Soc. Chim. France, No. 3-4, 272 (1947).

[13] S. Samson, L. G. Sillen, Ark. Kemi, 25A, No. 1 (1947).

[14] W. H. Zachariasen, Acta. Cryst., 1, 281 (1948).

[15] E. Wait, J. Inorg. Nucl. Chem., 1, 309 (1955).

[16] G. Bergstrom, G. Lundgren, Acta Chem. Scand., 10, 673 (1956).

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DEHYDROGENATION OF UNSYMMETRICAL METHYLISOPROPYLETHYLENE AND ITS MIXTURE WITH TETRAMETHYLETHYLENE

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In a continuation of our investigations of the dehydrogenation of tetramethylethylene and tertiary-butylethylene [3,3-dimethyl-1-butene] [1], we have studied the dehydrogenation of unsymmetrical methylisopropylethylene [2,3-dimethyl-1-butene] and also a mixture of it with tetramethylethylene over commercial catalysts used for the dehydrogenation of butylene to butadiene. The original hydrocarbons were prepared by the dehydration of pinacolyl alcohol [2]; the resulting mixture of unsymmetrical methylisopropylethylene and tetramethylene (boiling range 55-74°, $n^{20}D$ 1.4082, d^{20}_4 0.706) was separated by fractional distillation into unsymmetrical methylisopropylethylene (b.p. 55.8°/760 mm. $n^{20}D$ 1.3915, d^{20}_4 0.6825) and tetramethylethylene (b.p. 73°/760 mm, $n^{20}D$ 1.4122, d^{20}_4 0.708). The dehydrogenation experiments were carried out in a flow-type apparatus [1]; prior to a run, the catalyst was activated for an hour with hydrogen at 630°. Regeneration of the catalyst was carried out by passing a steam-air mixture through the catalyst bed at 630°. A temperature increase of 30-59° was observed during the regeneration of the K-16 catalyst. The dehydrogenation of unsymmetrical methylisopropylethylene was carried out over K-12, K-16, and K-18 catalysts at a temperature of 630°, a space rate of the order of 1500 liters per liter of catalyst per hour, and a steam dilution of eight. Generally, 5 ml of catalyst was used, and the duration of a run was 1 hour.

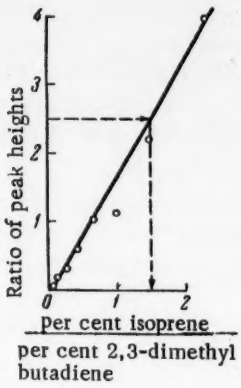

Fig. 1. Calibration curve for the apparatus.

Distillation of the condensate gave a fraction boiling at 32-72°; the dienic hydrocarbon content of this fraction was determined by condensation of the dienes with maleic anhydride [3]. In the condensates of all experiments on the dehydrogenation of unsymmetrical methylisopropylethylene, isoprene was identified by its addition product with maleic anhydride [4] (m.p. 64°) and 2,3-dimethyl-1,3-butadiene by its addition product with maleic anhydride [5] with a m.p. of 76° and by its tetrabromide [6] with a m.p. of 138.5-139°. Fractional distillation of the condensate of experiments on the dehydrogenation of this hydrocarbon over K-16 catalyst gave isoprene and 2,3-dimethyl-1,3-butadiene in a ratio of 1: 2. Distillation of the condensates obtained during the dehydrogenation of unsymmetrical methylisopropylethylene over K-18 and analysis of this condensate by gas-liquid chromatography both showed a ratio of isoprene: 2,3-dimethyl-1,3-butadiene of 1.4:1.

The gas-liquid chromatographic analyses of the condensates were carried out in a column with a diameter of 5 mm and a length of 2 meters; the column was packed with kieselguhr (particle diameters, 0.5-0.25 mm), which was wetted with dibutyl phthalate (14 g of dibutyl phthalate per 30 g of kieselguhr). The operating temperature of the column was 100°. Hydrogen was used as the carrier gas (10-15 ml/minute). A modified micro-flame detector [7,8] was used to detect hydrocarbon in the effluent gas.

The apparatus was first calibrated with synthetic mixtures (Figure 1).

Comparatison of the curve obtained by vapor-liquid chromatographic analysis of the condensate from Experiment VI (see Table 1) with curves corresponding to the analysis of synthetic mixtures (Figure 2) shows that the condensate contained trimethylethylene and uninvestigated isomerization products, probably 2- and

3-methylpentenes, in addition to isoprene, 2,3-dimetyl-1,3-butadiene, and unconverted feed. From a comparison of the chromatographic curves , it is seen that the condensate did not contain tetramethylethylene – a possible isomerization product of unsymmetrical methylisopropylethylene. An attempt to isolate it in the form of the dibromide by treatment of the condensate with Br_2 in chloroform also failed. The ratio of the heights of the isoprene and 2,3-dimethyl-1,3-butadiene peaks on the curve from the analysis of the condensate from Experiment VI (Figure 2, Curve a, Peaks Nos. 2 and 6) was 2.5, which corresponds to a ratio of these compounds in the condensate of 1.5:1 (Figure 1).

The total dienes as determined by gas-liquid chromatography was 23.0%, which is in good agreement with the data obtained by condensation with maleic anhydride (see Table 1). The results of the experiments on the dehydrogenation of unsymmetrical methylisopropylethylene are presented in Table 1.

TABLE 1

Catalyst	Expt. No.	Hydrocarbon fed, g	35-72° b.p. fraction, g.	Diene content, %	Amount of dienes, g	Diene yield % hydrocarbon fed
Dehydrogenation of unsymmetrical methylisopropylethylene						
K-16	X	27,60	21,70	16,35	3,55	12,85
	XII	28,00	21,10	16,50	3,48	12,45
K-12	I	26,90	16,75	17,7	2,96	11,45
	II	27,90	19,16	16,8	3,22	11,53
K-18	VI	30,7	12,60	23,9	3,15	10,25
	VII	30,7	13,83	24,7	3,42	10,80
Dehydrogenation of a mixture containing 30% unsymmetrical methylisopropylethylene and 70% tetramethylethylene						
K-16	III	31,8	23,46	17,7	4,15	13,05
	IV	31,8	23,51	16,6	3,93	12,30
K-12	I	29,0	19,9	23,3	4,63	15,95
	II	29,2	18,79	23,1	4,34	14,95
K-18	IV	31,9	23,08	22,7	5,24	16,80
	V	31,9	21,58	21,9	4,74	15,20

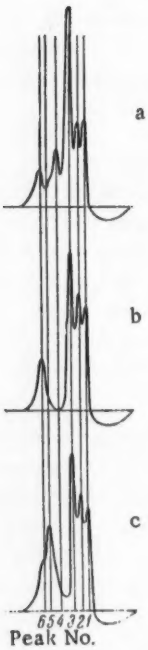

Fig. 2. Analysis of condensate by gas-liquid chromatography. a) Condensate from Experiment VI, b) synthetic mixture containing, in addition to unsymmetrical methylisopropylethylene and trimethylethylene 15% isoprene and 10% 2,3-dimethyl-1,3-butadiene, c) the same mixture with the addition of tetramethylethylene. Peak No. 1 corresponds to trimethylethylene, No. 2 – isoprene, No. 3 – unsymmetrical methylisopropylethylene, No. 4 – uninvestigated isomerization products, probably 2- and 3-methylpentenes, No. 5 – tetramethylethylene, No. 6 – 2,3-dimethyl-1,3-butadiene.

It may be seen from the data of Table 1 that dehydrogenation of this hydrocarbon over all three catalysts gives, under the conditions investigated, a stable yield of dienes (isoprene plus 2,3-dimethyl-1,3-butadiene) of the order of 10-13% of the hydrocarbons fed.

The dehydrogenation of a mixture of unsymmetrical methylisopropylethylene (30%) and tetramethylethylene (70%) was investigated under analogous conditions over K-12, K-16, and K-18 catalysts. The results obtained are presented in Table 1.

The effect of the composition of the hydrocarbon mixture on total diene yield was investigated with catalyst K-16. The behavior of the following mixtures was investigated: 10% unsymmetrical methylisopropylethylene ($n^{20}D$ 1.4118; d^{20}_4 0.7032), 30% ($n^{20}D$ 1.4012, d^{20}_4 0.706); 50% ($n^{20}D$ 1.4040, d^{20}_4 0.6925) and 75% ($n^{20}D$ 1.3975, d^{20}_4 0.683). The results obtained are presented in Figure 3.

It is seen that an increase in the unsymmetrical methylisopropylethylene content to 30% causes a sharp decrease in both the total yield of dienes and the

percentage content of dienes in the condensate. Further dilution of the tetramethylethylene with unsymmetrical methylisopropylethylene had less effect.

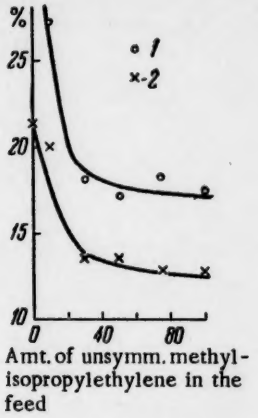

Fig. 3. Effect of feed composition on the dehydrogenation process. 1) Diene content in the condensate (wt.%), 2) yield of dienes, % of feed.

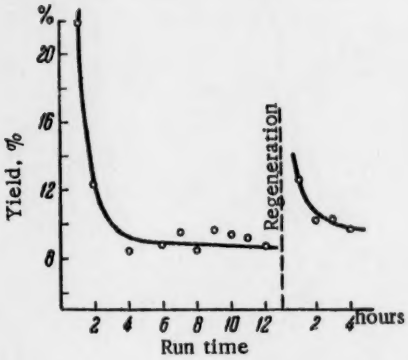

Fig. 4. Catalyst activity during several hours use without regeneration.

Catalyst K-16 was tested in a run of several hours duraction in which tetramethylethylene was dehydrogenated without intermediate catalyst regeneration. It was found that by the first hour of the experiment, the percentage content of diene in the condensate and the yield of 2,3-dimethyl-1,3-butadiene based on hydrocarbon fed had sharply decreased, but then remained relatively constant. These data show that regeneration of the catalyst with steam-air mixture should be carried out after each hour of operation. The catalyst which had been used for 12 hours without regeneration failed to return to its former activity after regeneration (see Figure 4).

LITERATURE CITED

[1] I. N. Nazarov, L. N. Ivanova and B. A. Rudenko, Proc. Acad. Sci. USSR, 118, No. 3, 509 (1958).*

[2] E. I. Erziutova, Alkylation of α- and β-Olefins with Tertiary Alkyl Halides in the Presence of $ZnCl_2$**; Candidate Dissertation, Inst. of Gen. Chem., Acad. Sci. USSR, 1954.

[3] A. I. Guliaeva et al., Analysis of the Products of the Production of Butadiene from Ethyl Alcohol by the S. V. Lebedev Method**, 1950, p. 195.

[4] J. Röeseken, M. J. F. de Rijck van der Gracht, Rec. Trav. Chim., 56, 1203 (1937).

[5] E. Farmer, F. Warren, J. Chem. Soc., 1929, 897.

[6] O. Sweeting, J. Johnson, J. Am. Chem. Soc., 68, 1057 (1946).

[7] R. Scott, Nature, 176, No. 4486, 793 (1955).

[8] J. Henderson, J. Knox, J. Chem. Soc., 1956, 2299.

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TRIS(TRIORGANOSILYL) VANADATES

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(Presented by Academician A. N. Nesmeianov, April 30, 1958)

Organic derivatives of vanadium remain almost unstudied. This is explained primarily by the fact that this element, having variously quantized valence electrons ($3d^3\ 4s^2$), does not tend to form stable organic compounds having a vanadium-carbon bond [1]. Compounds in which a vanadium atom is bonded to a carbon through an oxygen atom are known; however, they have not been sufficiently described [2].

In the present work, we studied the possibility of synthesizing organosilicon derivatives of vanadium containing a V—O—Si bond, tris(triorganosilyl) vanadates, which are presently unknown. These compounds were prepared by the interaction of triorganosilanols with V_2O_5, $VOCl_3$, or trialkyl vanadates, $OV(OR)_3$, as well as by the reaction of sodium triethylsilanolate with $VOCl_3$.

The simplest method for the preparation of tris(triorganosilyl) vanadates is by the reaction of vanadium pentoxide with triorganosilanols:

$$6R_3SiOH + V_2O_5 \rightleftarrows 2\,(R_3SiO)_3\,VO + 3H_2O, \qquad (1)$$

which is carried out under conditions such that the water formed is removed by continuous azeotropic distillation. Benzene or other suitable solvents may be used as the second component of the azeotropic mixture. Distillation of the water shifts the equilibrium of the reaction toward the formation of tris(triorganosilyl) vanadates, the yield of which comprises 50-80%.

Another simple method for the synthesis of triorganosilyl esters of orthovanadic acid is based on the reaction of vanadyl chloride with triorganosilanols in the presence of a hydrogen chloride acceptor (ammonia, tertiary amines, etc.):

$$3R_3SiOH + VOCl_3 + 3B \rightarrow (R_3SiO)_3\,VO + 3B \cdot HCl, \qquad (2)$$

where B is NH_3 (a); C_5H_5N (b). The yield of esters in this case is 60-80%.

A convenient method for the synthesis of organosilicon esters of orthovanadic acid is by transesterification of trialkyl vanadates with triorganosilanols in the presence of catalytic amounts of sodium derivatives of the latter (formed by the addition of metallic sodium):

$$3R'_3SiOH + (RO)_3\,VO \xrightarrow{R'_3SiO^-} (R'_3SiO)_3VO + ROH, \qquad (3)$$

where R is C_2H_5 (a), n-C_4H_9 (b); R' is CH_3, C_2H_5, C_6H_5. We have previously used, with success, the analogous reaction for the synthesis of organosilicon esters of boric [3] and orthotitanic* [4] acids. The reaction is carried out by distilling the alcohol from the reaction mixture, after which the reaction products are separated either by vacuum distillation or by recrystallization. The yield of tris(triorganosilyl) vanadates reaches 90%.

Finally, tris(triorganosilyl) vanadates can be prepared in good yield by the reaction of sodium triorganosilanolates with vanadyl chloride according to the reaction:

$$3R_3SiONa + VOCl_3 \rightarrow (R_3SiO)_3\ VO + 3NaCl. \qquad (4)$$

* Simultaneously with our preparation of tetrakis(triorganosilyl) titanates, other authors [5,6] also used the same route for the preparation of these compounds.

Tris(trialkylsilyl) vanadates are colorless, relatively mobile liquids with a weak trialkylsilanol odor; they are readily soluble in organic solvents. Tris(triphenylsilyl) vanadate is a crystalline material. It is interesting that the hydrocarbon analog of tris(trimethylsilyl) vanadate – tert-butyl vanadate, which we obtained in 10% yield by the reaction of V_2O_5 with $(CH_3)_3COH$ – is colorless crystalline material with a m.p. of 48° and a b.p. of 128-130°/20 mm. All tris(triorganosilyl) vanadates are insoluble in water, but they hydrolyze with the formation of the corresponding silanols and orthovanadic acid. The tendency toward hydrolysis decreases with an increase in the size of the organic radical bound to the silicon. It should be noted that the tris(triorganosilyl) vanadates have very poor thermal stability, which, however, is higher than that of the organic analogs. Thus, for example, tris(diethylphenylsilyl) vanadate decomposes to a significant extent with the formation of lower oxides of vanadium when distilled under a pressure of 2 mm. The other tris(triorganosilyl) vanadates behave similarly, although they decompose to a lesser extent.

The properties of the tris(triorganosilyl) vanadates synthesized are presented in Table 1.

EXPERIMENTAL

Starting reagents. The V_2O_5 was a commercial preparation (analytical grade). The $VOCl_3$ was prepared by reaction of vanadium pentoxide with thionyl chloride [7], b.p. 126°/758 mm. The triethyl vanadate was synthesized by the reaction of absolute ethyl alcohol with $VOCl_3$ in the presence of ammonia; b.p. 91°/11 mm, d^{20}_4, 1.1167; $n^{20}D$ 1.5103. Tri-n-butyl vanadate was obtained in 23% yield by refluxing, using a reflux condenser fitted with a water trap, a two-fold excess of n-butyl alcohol with benzene and vanadium pentoxide; b.p. 154-156°/10 mm, d^{20}_4, 1.0376, $n^{20}D$ 4915.* The triorganosilanols were prepared by a method described previously [4].

Analysis. The determination of silicon was carried out by wet combustion of a weighed amount of the material with a mixture of oleum and nitric acid. The precipitate of silicic acid was filtered and calcined at 900°. Vanadium was determined either by evaporation of the filtrate and subsequent calcination at 900°, or by hydrolysis of a separate weighed sample with an acidified water-alcohol mixture with subsequent evaporation of the solution and calcination of the V_2O_5 residue at 900°. The latter method was used for the analysis of the lower tris(triorganosilyl) vanadates.

All of the methods developed by us for the synthesis of tris (triorganosilyl) vanadates, Reactions (1)-(4), are illustrated below using as an example the preparation of tris(triethylsilyl) vanadate. Physical properties and analytical data for this compound, purified by redistillation under vacuum, are shown in Table 1 for each case. All of the remaining tris(triorganosilyl) vanadates were prepared similarly with the exception of tris(triphenylsilyl) vanadate, which was synthesized by Scheme (3) b in a medium of o-xylene, from which it was also recrystallized.

Synthesis by Scheme (1). A mixture of 3.64 g (0.02 mole) of V_2O_5, 15.9 g (0.12 mole) of triethylsilanol (b.p. 75°/24 mm, $n^{20}D$ 1.4340, d^{20}_4 0.8645), and 80 ml of benzene was heated at the boiling point for 2 hours, using a reflux condenser fitted with a water trap. About 1 ml of water had separated at the end of this time. The reaction mixture was filtered, and the filtrate, after distillation of the benzene, was fractionated under vacuum. 15.0 g (81%) of tris(triethylsilyl) vanadate was obtained; b.p. 188-192°/6 mm.

Synthesis by Scheme (2). a. 250 ml of benzene and 16.0 g (0.12 mole) of triethylsilanol were placed in a 500-ml three-necked flask fitted with a mechanical stirrer with a mercury seal, a dropping funnel, a reflux condenser, and a gas-inlet tube. A solution of 7.0 g (0.04 mole) of $VOCl_3$ in 50 ml of benzene was added dropwise, with stirring and cooling, to the first solution. Simultaneously, ammonia, purified by passage over solid KOH, was passed through the reaction mixture. The dropwise addition was carried out over a period of an hour at the rate such that the temperature of the reaction mixture did not exceed 8°. After the addition of all of the $VOCl_3$, ammonia was passed through the mixture for an additional 15 minutes. The reaction was completed by heating on a water bath at 80° for an hour. The reaction mixture was filtered, and the filtrate, after distillation of the benzene, was fractionated under vacuum. The yield of tris(triethylsilyl) vanadate was 10.0 g or 54.5%; b.p. 192-194°/7mm.

b. To a mixture of 16.0 g (0.12 mole) of triethylsilanol, 80 ml of benzene, and 8.7 g (0.11 g) of pyridine, cooled to −2°, was slowly added a solution of 7.0 g (0.04 mole) of $VOCl_3$ in 30 ml of benzene; the addition was carried out so that the temperature of the mixture did not exceed + 3°. After the addition of all of the $VOCl_3$, the reaction mixture was heated for to 70-80° over a period of 2 hours. The reaction mixture was cooled,

*As in original – Publisher's note.

filtered, and the filtrate, after distillation of the benzene, was distilled under vacuum. 14.0 g (76%) of tris (triethylsilyl) vanadate was obtained; b.p. 198-201°/13 mm.

TABLE 1

Tris(triorganosilyl) Vanadates

Compound	B.p., °C	Pressure, mm Hg	M.p. °C	d_4^{20}	n_D^{20}	Yield, %	Si, %		V, %		Preparation method
							Calc.	Found	Calc.	Found	
$[(CH_3)_3SiO]_3VO$	118—120	18	—	0,9812	1,4542	43,3	25,19	—	15,23	15,25 : 15,19	(1)
$[(CH_3)_2C_2H_5SiO]_3VO$	124—126	7	—	0,9802	1,4670	71,5	22,37	—	13,52	13,57 : 13,18	(3) a
$[(C_2H_5)_2CH_3SiO]_3VO$	169—170	5	—	0,9816	1,4730	38,6	20,13	20,06 : 20,03	12,17	12,18 : 12,02	(1)
	189—192	6	—	0,9830	1,4808	81,0	18,29	18,12 : 18,30	11,06	10,99 : 11,00	(1)
	182—185	5	—	0,9835	1,4828	94,0	18,29	18,11 : 18,39	11,06	11,36 : 11,13	(3) a
$[(C_2H_5)_3SiO]_3VO$	198—201	13	—	0,9825	1,4820	76,0	18,29	18,15 : 18,27	11,06	10,89 : 10,82	(2) b
	170—173	4	—	0,9837	1,4818	85,0	18,29	18,00 : 18,16	11,06	10,71 : 10,81	(4)
	192—194	7	—	0,9816	1,4812	54,5	18,29	18,00 : 18,36	11,06	11,02 : 10,86	(2) a
$[(C_2H_5)_2C_6H_5SiO]_3VO$	263—268	1,5	228	0,0767	1,5485	46,0	13,93	14,92 : 14,87	8,42	7,44 : 7,53	(1)
$[(C_6H_5)_3SiO]_3VO$	—	—		—	N_r 1,689*	90,0	9,43	9,18 : 8,86	5,70	5,51 : 5,62	(3) b
					N_p 1,664						

* Determined by immersion method.

Synthesis by Scheme (3). 6.1 g (0.032 mole) of triethyl vanadate, 13.2 g (0.1 mole) of triethylsilanol, and 0.005 g of metallic sodium were charged to a flask fitted with a herringbone dephlegmator. The mixture was slowly distilled until 4.0 g of ethyl alcohol had distilled at 78-84°. Vacuum fractionation of the residue gave 13.0 g (94%) of tris(triethylsilyl) vanadate with a b.p. of 182-185°/5 mm.

Synthesis by Scheme (4). 2.76 g (0.12 g-atom) of metallic sodium was added to a solution of 16.0 g (0.12 mole) of triethylsilanol in 400 ml of benzene. The mixture was refluxed for 8 hours until all of the sodium dissolved. 6.9 g (0.04 mole) of $VOCl_3$ in 15 ml of benzene was added to the triethylsilanolate while the mixture was stirred and cooled with ice water. The reaction mixture was then heated to 70-80° over a period of 2 hours. After separation of the sodium chloride and distillation of the benzene, the residue was fractionated under vacuum. 16.0 g (87%) of tris(triethylsilyl) vanadate was obtained; b.p. 184-194°/7 mm.

LITERATURE CITED

[1] A. N. Nesmeianov, Prog. Chem., 14, 261 (1945); E. G. Rochow, D. T. Hurd, R. N. Lewis, The Chemistry of Organometallic Compounds. N.Y., 1957, p. 236.

[2] M. G. Voronkov and Iu. I. Skorik, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1958, 503.*

[3] M. G. Voronkov and V. N. Zgonnik, J. Gen. Chem., 27, 1476 (1957). *

[4] B. N. Dolgov and N. F. Orlov, Proc. Acad. Sci. USSR, 117, 617 (1957); *Auth. Certif. 110,972 (1957).

[5] V. A. Zeitler, C. A. Brown, J. Am. Chem. Soc., 79, 4616, 4618 (1957); J. Phys. Chem., 61, 1174 (1957).

[6] D. C. Bradley, J. M. Thomas, Chem. Ind., No. 1, 17 (1958).

[7] H. Hecht, G. Jander, H. Schlapmann, Z. anorg. Chem., 254, 255 (1944).

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INVESTIGATION OF THE POLYMORPHISM OF N-ETHYL-3,4-DINITROPYRROLE

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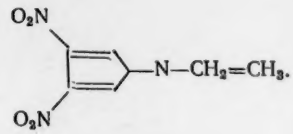
(Presented by Academician I. I. Chernaev, May 4, 1958)

We have studied a combination of methods for the phase analysis of the polymorphism of N-ethyl-3,4-dinitropyrrole:



The investigations were carried out by means of differential thermal analysis and by systematic dilatometric observations, and the thermal and volumetric effects of the transformations were studied in the temperature range from −100° to the melting point (105-108°). The results of the investigations show the presence of three reversibly transformed modifications of N-ethyl-3,4-dinitropyrrole. The lowest temperature form, III, is reversibly converted into form II at a temperature of 54-56° (see Figure 1a), and the latter form is, in turn, reversibly converted to phase I at 74-76°.

The differential cooling curves, which were recorded with an N. S. Kurnakov pyrometer, were taken while rapidly cooling centigram samples (micro method, cooling rate 3-3.5 degrees/ minute); the form of these curves (Figure 1a) shows that the transformation I → II is not fixed, while the transformation II → III appears with considerable clarity. In this connection, one's attention is attracted by the circumstance that the total endothermic effect on the heating curve during the transformations III→II and II→I (Figure 1a) is in agreement, to a close

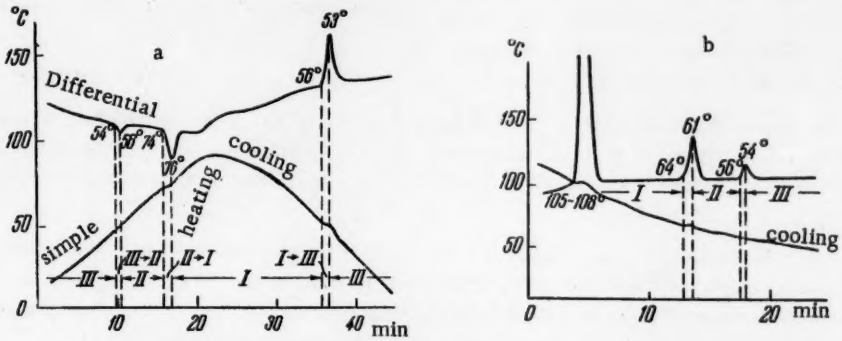


Fig. 1. Thermograms of N-ethyl-3,4-dinitropyrrole. a) with rapid heating and cooling, b) with slow cooling. I–III modifications.

approximation, with the absolute value of the effect of opposite sign (exothermic) in the temperature zone of the transformation II→III; this is caused by a retardation of the transformation I → II until a temperature of 55° is reached. It must be assumed that the phase transition I → III proceeds at this temperature. This is confirmed

by the fact that when the sample was again heated immediately after the conclusion of one heating-cooling cycle, the same two transitions occurred without change.

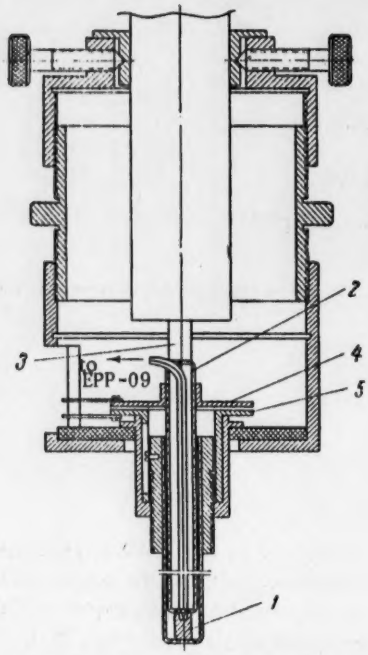


Fig. 2. Unit for simultaneously transmitting elongation to a capacitive transducer and to the mechanical optical system of an optical measuring system. Explanation in text.

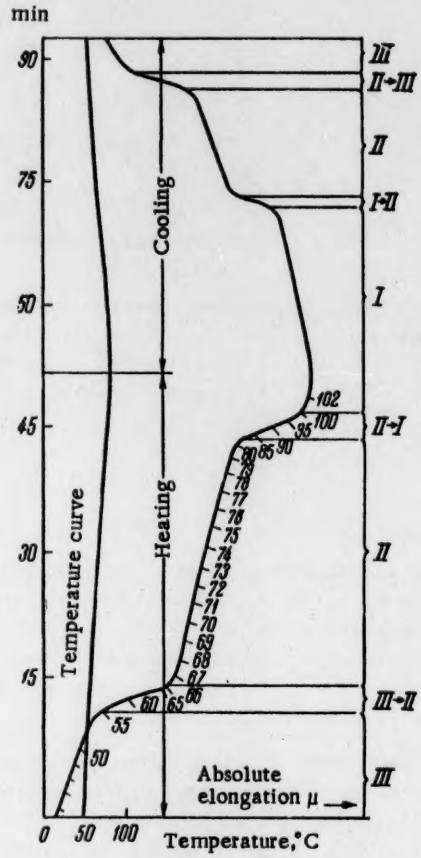


Fig. 3. Dilatometric curve recorded on the automatic electronic dilatometer combined with an optical measuring system. I–III modifications.

In separate cases at lower cooling rates, we were able to obtain curves of a somewhat different form where the heat effect of the transition I → II was separate from the heat effect of the transition II → III; however, the limits of the transformation I → II were invariably shifted downward along the temperature axis, and the effect became fixed, not at a temperature of 74°, but at 60-65° (see Figure 1b).

Thus, differential thermal analysis, which permits objectively fixing the results of very rapid (nonequilibrium) cooling of small samples, recorded a substantial shift in the temperature of the phase transition I → II (in comparison with the temperature of II → I) as a function of the cooling conditions and the previous history of the sample.

This temperature hysteresis in the phase transitions I → II showed up especially clearly on the dilatometric curves, which we obtained both visually and by automatic recording using a complex dilatometric apparatus consisting of an A. V. Panov electronic dilatometer and an IKV vertical optical measuring system. In this work, the samples were of cylindrical form with a diameter of 4 mm and a length of 4.55 mm.

Rather than dwell on the details of the construction of the electronic dilatometer [1] or of the dilatometer based on the optical measuring system [2], which have already appeared in print, we shall limit ourselves to a brief description of a unit which we developed for combining the apparatus to permit visual reading of the absolute elongations and to permit relating these readings to the automatically recorded couse of the temperature and dilatometric curves, which are registered from the capacitive transducer of the A. V. Panov dilatometer by means of an EPP-09 recording potentiometer. As seen from Figure 2, the thermal expansion of sample 1 is

transmitted to inner quartz tube 2,which then moves the measuring rod 3 of the optical system in a vertical direction and simultaneously changes the position of the movable upper plate 4 of the capacitive transducer relative to the stationary lower plate 5.

The electronic dilatometer of A. V. Panov, which possesses a high sensitivity of the order of 10^{-5} mm and which permits dilatometric measurements at very high heating rates, gives only a qualitative picture of the dilatometric effects during phase transitions, and is inconvenient for directly characterizing these effects quantitatively. Therefore, the combination of this dilatometer with the optical measuring system into a single apparatus makes it possible to eliminate this deficiency and to obtain completely specific data, thereby permitting ready calculation both of the value of the linear contractions during phase transitions and of the coefficients of linear expansion of the separate phases.

In Figure 3 are shown the temperature and dilatometric curves which were recorded on the chart of the EPP-09. Heating was carried from room temperature to a temperature close to the melting point, after which the sample was cooled. Regions of the existence of phases I, II, and III and of the phase transitions III→II and II→I as well as I→II and II→III clearly appeared during both heating and cooling at temperatures in agreement with the data from differential thermal analysis (see Figure 1). The absolute elongation during the experiments was noted directly on the dilatometric curve, which was automatically recorded from the capacitive transducer. This permitted us to obtain the values of the linear contractions during phase transitions immediately at the time of the measurements, since additional treatment of the data was not required.

As may be seen from the dilatometric curves, the reversible phase transformations III→II and II→I are accompanied by a considerable increase in the linear dimensions; this was especially noticeable for the transformation II→I, where it was of the order of 0.6% of the dimensions of the sample.

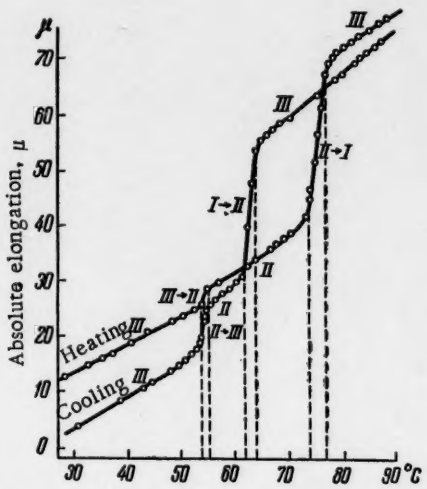


Fig. 4. Dilatometric curves of the hysteresis of the I–II transformation: obtained with the optical system.

The form of the curves obtained by means of the vertical optical measuring system alone (see Figure 4) was identical in principle with the form of the curves recorded with the electronic dilatometer.

This permitted us to confine ourselves to visual observations of the dilatometric effects of the transformations during further measurements, and this made it possible to take a dilatometric curve with a sample, the temperature of which was thermostatically controlled at different temperatures.

Considerable interest is attached to a comparison of the dilatometric expansion curves (heating) with the dilatometric contraction curves (cooling, which were alternately recorded for the same sample. It is noted that the dilatometric expansion curve usually reproduced, to a good approximation, the previously obtained cooling curve. In addition, in all cases, the hysteresis region of the phase transition I⇌II showed up excellently, and we were able to narrow this region down by holding the sample for a sufficient length of time in the temperature zone of the transformation.

It is possible that the hysteresis in the transformation I⇌II is due to a significant difference in the relative changes in specific volumes of the phases (as compared to the transformation II⇌III). The average value of the relative change in volume during the transition I⇌II was 1.8%, while in the transition II⇌III it was only 0.4%. In this connection, it is interesting to note that, as indicated by N. N. Sirota [3], the difference in the relative changes in the specific volumes of the phases exerts a considerable effect on the magnitude of the hysteresis of the transformation, since it appears as a squared term in the equation which defines the effect of a number of physical and thermodynamic characteristics of the substance on the magnitude of the hysteresis.

There is no doubt that the similar hysteresis in the transformations, a hysteresis due to the nonequilibrium phase transitions of N-ethyl-3,4-dinitropyrrole, is, as we have previously pointed out [4], a very typical phenomenon for other organic substances also.

In conclusion, we take this opportunity to express our appreciation to Prof. C. C. Novikov for the gift of the sample of N-ethyl-3,4-dinitropyrrole.

LITERATURE CITED

[1] I. N. Kidin and A. V. Panov, Factory Labs., No. 1, 48 (1957).

[2] L. A. Gaivaronskii and K. V. Popov, Factory Labs, No. 8, 986 (1953).

[3] N. N. Sirota, Proc. Acad. Sci. USSR, 59, No. 7, 1309 (1948).

[4] G. B. Ravich, Prog. Chem., 21 , No. 9, 1117 (1952).

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SYNTHESIS OF SOME ORGANOSILICON AND ORGANOSILICOTITANIUM COMPOUNDS

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During an investigation of the effect of triaryl-, trialkyl-, and mixed tri(alkylaryl)siloxy groups on the properties of organosilicotitanium compounds, we found it necessary to synthesize certain new organosilicotitanium derivatives containing aromatic and aliphatic radicals attached to the silicon. Methods for the synthesis of tetrakis (trimethylsiloxy) titanium [1,2] and tetrakis(triphenylsiloxy) titanium [3,4] have previously been described in the literature. For the preparation of mixed tetrakis(tri(arylalkyl) siloxy) titanium compounds, we synthesized a number of organosilicon compounds, which were the starting materials for the preparation of the tetrakis(tri(alkylaryl)siloxy) titanium compounds. Phenyldimethylchlorosilane and methyldiphenylchlorosilane were prepared by Grignard reactions. With the aim of obtaining the alkylarylsilanols, the chlorosilanes were converted to the acetates, and these were then hydrolyzed with ammonia solutions. The overall scheme of the reactions used for the preparation of alkylarylsilanols can be represented by the following equations:

$$\text{I. } C_6H_5MgBr + C_6H_5CH_3SiCl_2 \rightarrow (C_6H_5)_2CH_3SiCl + MgBrCl;$$

$$\text{II. } (C_6H_5)_2CH_3SiCl + CH_3COOK \rightarrow (C_6H_5)_2CH_3SiOCOCH_3 + KCl;$$

$$\text{III. } (C_6H_5)_2CH_3SiOCOCH_3 + NH_4OH \rightarrow CH_3(C_6H_5)_2SiOH + CH_3COONH_4.$$

All of the compounds prepared in this sequence of reactions were isolated at each stage of the process, and their elemental compositions and basic properties were determined. The properties of the compounds synthesized are presented in Table 1.

TABLE 1

Compound	Formula	B.p.°C/ mm Hg	n_D^{20}	d_4^{20}	MR		Yield, %
					Found	Calc.	
Methyldiphenylchlorosilane	$CH_3(C_6H_5)_2SiCl$	146—153/10	1,5742	1,1277	68,4	69,06	54,4
Dimethylphenylchlorosilane	$(CH_3)_2C_6H_5SiCl$	97—100/33	1,5184	1,0646	48,8	49,93	63,3
Methyldiphenylacetoxysilane	$CH_3(C_6H_5)_2SiOCOCH_3$	132—135/2	1,5530	1,0756	75,95	75,91	51,2
Dimethylphenyl acetoxysilane	$(CH_3)_2C_6H_5SiOCOCH_3$	92—95/7	1,4907	1,0065	55,79	55,78	59,1
Methyldiphenylsilanol	$CH_3(C_6H_5)_2SiOH$	130—134/2	1,5812	1,0829	65,80	66,42	67,8
Dimethylphenylsilanol	$(CH_3)_2C_6H_5SiOH$	192—195/7	1,5108	0,9848	46,11	46,10	65,1
Tetrakis (methyldiphenylsiloxy) titanium	$[CH_3(C_6H_5)_2SiO]_4Ti$	370—374/6	1,5960	1,1248	273,4	274,8	35,8
Tetrakis(dimethylphenylsiloxy) titanium	$[(CH_3)_2(C_6H_5)SiO]_4Ti$	274—275/7	1,5392	1,0533	193,97	193,476	51,9

The preparation of the tetrakis(tri(alkylaryl)siloxy)titanium compounds was carried out by two methods. The action of titanium tetrachloride on diphenylmethylsilanol in the presence of ammonia

$$4\,(C_6H_5)_2\,CH_3SiOH + TiCl_4 + 4\,NH_3 \rightarrow [(C_6H_5)_2\,CH_3SiO]_4\,Ti + 4\,NH_4Cl$$

gave tetrakis(diphenylmethylsiloxy) titanium, which was a liquid at room temperature and which had a high boiling point.

Tetrakis(dimethylphenylsiloxy) titanium was prepared by the reaction of sodium dimethylphenylsilanolate with titanium tetrachloride according to the scheme:

$$2\,(CH_3)_2\,C_6H_5SiOH + 2\,Na \rightarrow 2\,(CH_3)_2\,C_6H_5SiONa + H_2;$$
$$4\,(CH_3)_2\,C_6H_5SiONa + TiCl_4 \rightarrow [(CH_3)_2\,C_6H_5SiO]_4\,Ti + 4NaCl.$$

The properties of these compounds are presented in Table 1.

EXPERIMENTAL

Dimethylphenylchlorosilane. 12 g of magnesium and 200 ml of ether were charged to a three-necked flask fitted with a stirrer, a reflux condenser, and a thermometer. A solution of 87 g of bromobenzene in 50 ml of ether was added to the flask from a dropping funnel. The temperature was held at 34-38° until the magnesium was completely dissolved. The resulting Grignard reagent was introduced into a solution of 77 g of dimethyldichlorosilane in 70 ml of ether. The reaction proceeded at 38-44°. After decantation from the precipitate, the reaction products were distilled. 63.68 g yield, (63.3% of theoretical) of a fraction boiling at 97-100° / 33 mm was separated.

Found % Cl 20.5 $C_8H_{11}SiCl$. Calculated %: Cl 20.8.

Methyldiphenylchlorosilane. The synthesis of methyldiphenylchlorosilane was carried out similarly to the synthesis of dimethylphenylchlorosilane. 157 g of bromobenzene, 24 g of magnesium, and 191 g of methylphenylchlorosilane gave, after vacuum fractionation, a fraction boiling at 146-153° / 10 mm; the yield was 125.15 g (54.4% of theoretical).

Literature data [5, 6]: methyldiphenylchlorosilane, b.p. 180-195° / 45 mm.

Found %: Cl 15.9 $C_{13}H_{13}SiCl$. Calculated %: Cl 15.3.

Methyldiphenylacetoxysilane. 9.8 g of potassium acetate in 100 ml of dry toluene was charged to a three-necked flask. From a dropping funnel was added 23.25 g of methyldiphenylchlorosilane at a temperature of 18-28°. The mixture was then stirred and heated at 70-80° for 18-20 hours. The precipitated KCl was filtered, the solvent distilled, and the remaining liquid was distilled under vacuum at 132-135° / 2 mm. The yield was 12.95 g (51.2% of theoretical); $n^{20}D$ 1.5530; d^{20}_4 1.0756; found MR 75.95; calculated MR 75.91.

Found %: C 70.32; H 6.84; Si 10.86 $C_{15}H_{16}O_2Si$. Calculated %: C 70.31; H 6.25; Si 10.93.

Dimethylphenylacetoxysilane. This compound was prepared similarly from 63.68 g of dimethylphenylchlorosilane and 42 g of potassium acetate in 150 ml of dry toluene. Vacuum distillation gave 57.17 g of dimethylphenylacetoxysilane with a b.p. of 92-95° / 7 mm. The yield was 59% of theoretical; $n^{20}D$ 1.4907; d^{20}_4 1.0065; found MR 55.79; calculated MR 55.78.

Found %: C 61.43; H 7.28; Si 14.08 $C_{10}H_{14}O_2Si$. Calculated %: C 61.85; H 7.22; Si 14.40.

Methyldiphenylsilanol. 100.5 ml of 15% NH_4OH (sp. gr. 0.944) and 120 ml of ether were charged to a flask equipped with a stirrer, a thermometer, and a dropping funnel. The mixture was cooled with ice to 0°, and was held at this temperature during the entire course of the reaction. 96.6 g of methyldiphenylacetoxysilane in 100 ml of ether was added from the dropping funnel over a period of 30-40 minutes; the mixture was stirred during the addition. After the acetate had been added, stirring was continued for another 40-50 minutes, after which the layers were separated. The ether layer was washed twice with water (60 ml), and dried over calcined Na_2SO_4. After distillation of the ether, the residue was fractionated under vacuum. The fractionation yielded a

fraction with a b.p. of 130-134°/2 mm; yield 54.26 g (67.8% of theoretical): $n^{20}D$ 1.5812; d^{20}_4 1.0829; found MR 65.80; calculated MR 66.42.

Found %: C 72.98; H 6.84; Si 13.00 $C_{13}H_{14}OSi$. Calculated %: C 72.89; H 6.54; Si 13.07.

Dimethylphenylsilanol. This compound was prepared similarly by hydrolysis of 57 g of dimethylphenylacetoxysilane in 80 ml of 15% NH_4OH (sp. gr. 0.944). Distillation gave a fraction with a b.p. of 192-197°/mm; yield 29.02 g (65.1% of theoretical); $n^{20}D$ 1.5108; d^{20}_4 0.9848; found MR 46.11; calculated MR 46.10.

Found %: C 63.17; H 8.09; Si 18.01 $C_8H_{13}OSi$. Calculated %: C 63.15; H 8.00; Si 18.42.

Sodium dimethylphenylsilanolate. 27 g of the silanol in 30 ml of dry benzene was charged to a three-necked flask fitted with a stirrer, a thermometer, and a reflux condenser. 4.05 g of metallic sodium was added slowly to the flask added piece by piece; the reaction was carried out at 49-51°. After the addition of 1/3 of the total amount of sodium, the temperature dropped to 25°. The reaction mixture was heated for 2 hours at 50°. The 2.4 g of residual sodium was filtered. The resulting solution of sodium silanolate was used directly in further syntheses. The yield of silanolate was 44% of theoretical. The concentration of the solution was determined by titration of an aliquot with 0.1 N HCl.

Tetrakis(methyldiphenysiloxy) titanium. 12.84 g of methyldiphenylsilanol in 180 ml of dry benzene was charged to a three-necked flask fitted with a stirrer, a reflux condenser, and a tube for the introduction of ammonia. The mixture was cooled with ice to a temperature of 0-2°. 2.85 g of $TiCl_4$ in 20 ml of dry benzene was added dropwise, with stirring, to the solution, through which NH_3 was passed. At first, the mixture became bright yellow, but then, on further addition of $TiCl_4$, this color disappeared. After the dropwise addition of the $TiCl_4$ was concluded, ammonia was passed through the solution for another 30 minutes, and the solution was then heated for 3 hours to remove excess ammonia. The precipitate was filtered, and the benzene distilled. The residue – a yellow, viscous liquid – was distilled under vacuum; a fraction with a b.p. of 370-374°/6 mm was collected; yield 4.05 g (35.8% of theoretical); $n^{20}D$ 1.5960; d^{20}_4 1.1248; found MR 273.4; calculated MR 274.8.

Found %: C 69.19; H 6.68; Si 12.51; Ti 5.33 $C_{52}H_{52}OSi_4Ti$. Calculated %: C 69.40; H 5.78; Si 12.43; Ti 5.33.

Tetrakis(dimethylphenylsiloxy) titanium. 24 g of a 25% benzene solution of sodium dimethylphenylsilanolate was charged to a three-necked flask. To this was added dropwise and slowly 1.64 g of $TiCl_4$ in 10 ml of dry benzene. The reaction proceeded exothermally and the temperature rose to 28-42°. The dropwise addition of $TiCl_4$ was continued to a neutral reaction of the medium. The voluminous precipitate of NaCl was filtered, and the benzene was distilled from the filtrate. Vacuum fractionation of the residual liquid gave a fraction with a b.p. of 274-275°/7 mm; yield 2.7 g (51.9% of theoretical); $n^{20}D$ 1.5392; d^{20}_4 1.0533; found MR 193.97; calculated MR 193.476.

Found %: C 59.00; H 7.54; Si 16.81; Ti 6.71. $C_{32}H_{44}O_4Si_4Ti$. Calculated % C 58.99; H 6.75; Si 17.18; Ti 7.36.

LITERATURE CITED

[1] W. D. English, L. H. Sommer, J. Am. Chem. Soc., 77, 170 (1955).

[2] K. A. Andrianov, A. A. Zhdanov, N. A. Kurasheva and V. G. Dulova, Proc. Acad. Sci. USSR, 122, 1050 (1957).*

[3] V. A. Zeitler, C. A. Brown, J. Am. Chem. Soc., 79, 17, 4616 (1957).

[4] B. N. Dolgov and N. F. Orlov, Proc. Acad. Sci. USSR, 117, 617 (1957).*

[5] C. A. Burkhard, R. Krieble, J. Am. Chem. Soc., 69, 2687 (1947).

[6] F. C. Whitmore et al., J. Am. Chem. Soc., 69, 2108 (1947).

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COMPOUNDS OF BERYLLIUM OXYACETATE WITH SULFUR DIOXIDE

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The literature concerned with addition compounds of beryllium oxyacetate has primarily reported compounds with substances containing amine nitrogen [1-3]. These compounds are fairly stable, and are probably formed through the pair of free electrons of the nitrogen. However, $Be_4O(CH_3COO)_6$ would also be expected to form compounds with weaker bonds, compounds of the type of the so-called "inclusion compounds" [4]. Pavell, in a report at the international conference on complex compounds in 1956 [5], reported on the possibility of the formation of such compounds by beryllium oxyacetate.

The compound of beryllium oxyacetate with sulfur dioxide, the preparation of which was the subject of an earlier, brief communication [2], is probably a compound of this type. In the present article are presented the results of a more detailed investigation of the interaction of beryllium oxyacetate with sulfur dioxide. The compound of $Be_4O(CH_3COO)_6$ with SO_2 may be isolated as well-formed octahedra by evaporation of a solution of beryllium oxyacetate in liquid sulfur dioxide. This compound is extremely unstable at room temperature, and rapidly decomposes to beryllium oxyacetate and sulfur dioxide; therefore, its isolation and the accurate determination of its composition by ordinary methods of chemical analysis is difficult.

The method selected by us for the study of the interaction of beryllium oxyacetate with sulfur dioxide was the construction of composition—vapor pressure diagrams at constant temperature for the system $Be_4O(CH_3COO)_6$—SO_2. The tensimeter-eudiometer of Huttig [6] was used for this purpose; this apparatus permitted us to carry out simultaneously phase composition and pressure measurements. The method was as follows. A known amount of sulfur dioxide, sufficient to dissolve the beryllium oxyacetate, was added to a weighed sample of about 800 mg of beryllium oxyacetate in a 10-ml reaction cell, which was contained in a constant temperature bath; sulfur dioxide was then transferred portion-wise from the reaction cell to a previously evacuated space of known volume which was connected to the reaction cell. The pressure in the system was measured by a mercury manometer. Thus, knowing the volume and the pressure, it was possible to calculate each time the amount of sulfur dioxide removed, and to determine the composition of the mixture. Equilibrium was attained in the system after 10-20 hours (in different experiments). In Figure 1 are presented the composition — pressure isotherms obtained at −9.5, −15, −20, and −30°.

From the general form of the isotherm, it follows that during the evaporation of a saturated solution of $Be_4O(CH_3COO)_6$ in liquid sulfur dioxide, a compound having the composition $Be_4O(CH_3COO)_6 \cdot 2SO_2$ separates. Thus, it was established that the compound of the composition $3Be_4O(CH_3COO)_6 \cdot 4SO_2$, previously described by us in reference [2], is a product of the partial decomposition of the compound of beryllium oxyacetate with two molecules of sulfur dioxide. In addition to the compound with a 2:1 composition, the 1:1 compound, $Be_4O \cdot (CH_3COO)_6 \cdot SO_2$, was observed to exist in the system; this compound is formed by the decomposition of the 2:1 compound. No other compounds were found in the temperature range from −10 to −30°. The stability of the compounds decreased with an increase in temperature, as is indicated by the increasing slope of the plateaus on the isotherms. At −10, the decomposition of the compounds proceeds, as before, in two stages, but by the formation of a phase of variable composition.

The values of the SO_2 pressures corresponding to the compositions of the 2:1 and 1:1 compounds were used to obtain the function $\lg P = f\,\frac{1}{T}$. The dependence of the dissociation pressures of the compounds on temperature is shown graphically in Figure 2. The dependence of the SO_2 pressure on temperature in the system

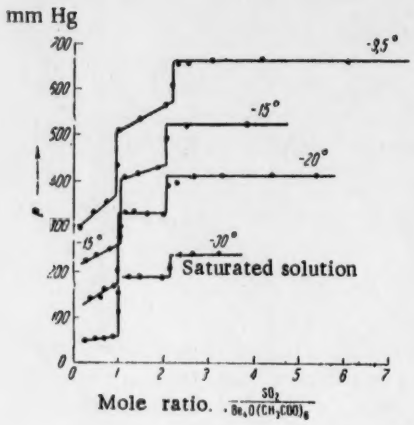

Fig. 1. Isothermal vapor pressure curves for SO_2 in the system $Be_4O(CH_3COO)_6 - SO_2$.

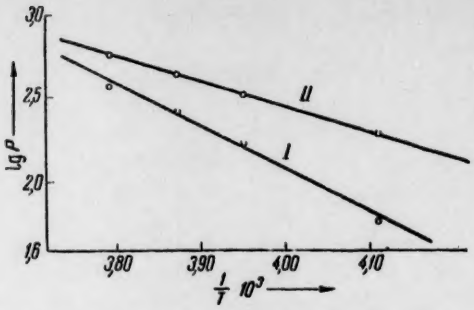

Fig. 2. Change in dissociation pressure of the compounds $Be_4O(CH_3COO)_6 \cdot SO_2$ (I) and $Be_4O(CH_3COO)_6 \cdot 2SO_2$ (II) with temperature.

$$Be_4O(CH_3COO)_6 \cdot SO_2 \rightleftarrows Be_4O(CH_3COO)_6 + SO_2$$

can be expressed by the equation $\lg P = -\frac{2507.68}{T} + 12.10$ when $\Delta H_1 = -Q_{p_1} = 11.47$ kcal/mole in the temperature interval from 243 to 263°.

The dependence of SO_2 pressure on temperature in the system

$$Be_4O(CH_3COO)_6 \cdot 2SO_2 \rightleftarrows Be_4O(CH_3COO)_6 \cdot SO_2 + SO_2$$

is described by the equation $\lg P = -\frac{1525,44}{T} + 8.54$, and $\Delta H_2 = -Q_{p_2} = 6.98$ kcal/mole in the temperature interval from 243 to 263°. The overall equation for the reaction forming $Be_4O(CH_3COO)_6 \cdot 2SO_2$, taking into account the heat of reaction, is:

$$Be_4O(CH_3COO)_6 + 2SO_2 = Be_4O(CH_3COO)_6 \cdot 2SO_2 + 18,45 \text{ kcal.}$$

The average heat of formation is 9.22 kcal per mole of SO_2.

Thus, the value of the heat of formation is lower than usual for coordination compounds; it is approximately the same as for the inclusion compounds of urea [4], 5-10 kcal/mole; hydroquinone [5], 9-10 kcal/mole; cyclodextrin compounds [4], 12 kcal/mole. It should be pointed out here that the heat of vaporization of sulfur dioxide is 6.32 kcal/mole. In this connection, it is also noted that at −10° (the boiling point of SO_2), the compounds have the character of solid solutions, and can exist only at increased pressures of sulfur dioxide. At temperatures above 10°, crystals of $Be_4O(CH_3COO)_6 \cdot 2SO_2$ melt in sealed tubes.

We also carried out an x-ray investigation of the compound $Be_4O(CH_3COO)_6 \cdot 2SO_2$ using the oscillating crystal method; an RKOP camera was used with Cu radiation from a BSVL-type tube. The x-ray exposures were carried out at a temperature of 0-3°, and the monocrystal was sealed in a thin-walled Pyrex glass capillary.

The compound $Be_4O(CH_3COO)_6 \cdot 2SO_2$ crystallizes in a cubic, diamond lattice with an identity period of a = 17.1 A. The density, which was determined at −12° by the method of equal weighings in an ethyl bromide-dichloroethane mixture, is 1.43; the x-ray density is 1.42. It is evident that the crystal structure of $Be_4O(CH_3COO)_6 \cdot 2SO_2$ is very close to the crystal structure of pure beryllium oxyacetate, and can be considered as derived from it— with some expansion of the lattice from 15.7A for pure beryllium acetate to 17.1 A for the binary compound.

A comparison of the data on the composition and properties of the compound permits the following picture to be drawn of the structure of this substance.

According to Pauling and Sherman [7], the beryllium oxyacetate molecule has four "wineglasses" — depressions — distributed on the faces of the Be_4O tetrahedron. Owing to the existence of similar depressions in the crystal

lattice of cubic beryllium oxyacetate, there are closed hollows, and there must be two hollows on each molecule of beryllium oxyacetate. It can be visualized that, during crystallization from solution, molecules of sulfur dioxide are included in these hollows: at the same time, there is an expansion of the crystal lattice in comparison with the lattice of beryllium oxyacetate. A compound of the type $Be_4O(CH_3COO)_6 \cdot 2SO_2$ is formed when the hollows are completely filled, while when the hollows are incompletely filled, the compound is of the type of $Be_4O(CH_3COO)_6 \cdot SO_2$. No forces other than the usual intermolecular van der Waals forces act on a molecule of SO_2 included in a hollow. This explains the comparatively low heat of formation of the compounds $Be_4O \cdot (CH_3COO)_6 \cdot 2SO_2$ and $Be_4O(CH_3COO)_6 \cdot SO_2$. Therefore, compounds of beryllium oxyacetate with sulfur dioxide can be considered as true clathrate compounds of the type of clathrates of hydroquinone with SO_2 or CH_3OH [4,5].

LITERATURE CITED

[1] H. Steinmetz, Z. anorg. Chem., 54, 217 (1907).

[2] A. I. Grigor'ev, A. V. Novoselova and K. N. Semenenko, J. Inorg. Chem., 2, 1374 (1957).

[3] A. I. Grigor'ev, A. V. Novoselova and K. N. Semenenko, J. Inorg. Chem. 3, 1599 (1958).

[4] F. Kramer, Inclusion Compounds, Foreign Lit. Press, 1958. (Russian Translation).

[5] H. M. Pavell, Rec. Trav. Chim., 75, 885 (1956).

[6] G. F. Huttig, Z. anorg. Chem., 114, 161 (1920).

[7] L. Pauling, J. Sherman, Proc. Nat. Acad. Sci., 20, 340 (1934).

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THE SOLUBILITY OF SILICON TETRAIODIDE IN NONAQUEOUS SOLVENTS

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The recrystallization of silicon tetraiodide from nonaqueous solvents is one of the important steps in the purification of it during the production of silicon of high purity. This has stimulated interest in the study of the solubility of silicon tetraiodide in nonaqueous solvents.

The solubility data available from the literature [1,2] is limited; therefore, it seemed of interest to study systematically the solubility of silicon tetraiodide in nonaqueous solvents. The solvents used were benzene, toluene, xylene, cyclohexane, chloroform, carbon tetrachloride, normal octane, and silicon tetrachloride.

The silicon tetraiodide was prepared by direct synthesis from technical silicon of 98% purity and analytical grade iodine; the product was recrystallized from benzene, and sublimed under vacuum. The resulting silicon tetraiodide contained Al $2 \cdot 10^{-4}$, Fe $5 \cdot 10^{-5}$, Ti $< 1 \cdot 10^{-4}$, Mg $< 1 \cdot 10^{-5}$, Ca $< 1 \cdot 10^{-5}$, Cu $< 1 \cdot 10^{-5}$ and Zn $< 1 \cdot 10^{-4}$ wt. %. The aluminum was determined polarographically; the iron, titanium, copper, magnesium, calcium, and zinc were determined colorimetrically. The silicon tetraiodide crystals were white with a slight greenish cast.

The following solvents of the indicated purity were used: benzene (thiophene free); toluene, chloroform, carbon tetrachloride, and silicon tetrachloride, all analytical grade; and pure grade n-octane. The cyclohexane (pure grade) was additionally purified, and had a melting point of 6.2°.

The solubilities were determined by the method of Alekseev [3]. In order to protect the silicon tetraiodide from hydrolysis by atmospheric moisture, all of the preparative work was carried out in a hermetically sealed compartment purged with dry nitrogen.

Weighed portions of silicon tetraiodide and solvent were charged to tubes with intakes. A small, glass-encased, iron cylinder was placed in each tube. The contents of the tube were frozen; the nitrogen remaining from the charging operation was pumped out, and the tube was sealed.

Constant temperature was maintained by means of a thermostatted oil bath. The temperature was controlled by means of a contact thermometer with an accuracy of ±0.1°. For stirring the contents of the tube, the oil bath was equipped with a special magnetic device, which imparted a rapid reciprocating motion to the iron cylinder contained in the tube. At temperatures close to that at which the solid phase disappeared, stirring was continued for 3-4 hours. Preliminary experiments showed that this time was quite sufficient for establishing equilibrium between the liquid and solid phases.

The solubility curves of silicon tetraiodide are presented in Figure 1.

Our results from the determination of the solubility of silicon tetraiodide in toluene differ sharply from those presented in reference [2]. These data show a solubility for silicon tetraiodide in toluene at 20° of 3.2 wt. %, while according to our data, the solubility at 25° is 33 wt.%. It may be asserted that the solubilities of silicon tetraiodide in toluene cited in reference [2] are clearly in error.

The nature of the curves permit the assumption that the solutions studied are regular.

Hildebrand [4] derived the following equation for regular solutions:

$$RT \ln \frac{a_2}{N_2} = v_2 \left(\frac{N_1 v_1}{N_1 v_1 + N_2 v_2} \right)^2 \left[\left(\frac{\Delta E_2}{v_2} \right)^{1/2} - \left(\frac{\Delta E_1}{v_1} \right)^{1/2} \right]^2, \qquad \text{(A)}$$

where a_2 is the activity, N_1 and N_2 are mole fractions, v_1 and v_2 are molar volumes, ΔE_1 and ΔE_2 are molar energies of vaporization.

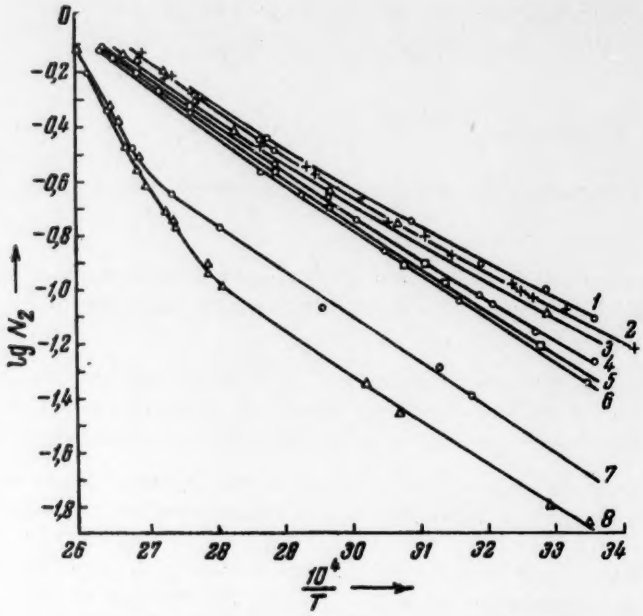

Fig. 1. Solubility of silicon tetraiodide in nonaqueous solvents. 1) Toluene 2) benzene, 3) xylene, 4) chloroform, 5) carbon tetrachloride, 6) cyclohexane, 7) normal octane, 8) silicon tetrachloride.

TABLE 1
Solutions of Silicon Tetraiodide at 25°

Solvent	Dipole moment $\times 10^{18}$ e.s.u.	Mole fract. of silicon tetraiodide	$(\Delta E_1/v_1)^{1/2}$, (cal./cc)	$(\Delta E_2/v_2)^{1/2}$, (cal./cc)
Toluene	0,4	0,0776	8,9	12,03
Benzene	0	0,0707	9,15	12,38
Metaxylene	0,3	0,0661	8,8	11,92
Chloroform	1,1	0,0525	9,3	12,66
Carbon tetrachloride	0	0,0467	8,6	11,97
Cyclohexane	0	0,0427	8,2	11,56
n-Octane	0	0,0146	7,55	11,21
Silicon tetrachloride	0	0,0126	7,6	11,49
			Average. . . .	11,90

In order to calculate $(\Delta E_2 / v_2)^{1/2}$, for silicon tetriodide (Table 1), it is necessary to insert into Equation

the experimental solubility values, using the ideal solubility in place of a_2. The ideal solubility was calculated from the Schroeder-Le Chatelier equation. Our determination of the melting point of silicon tetraiodide gave a value of 123.5-123.8°. For the heat of fusion, we used 1200 cal. / mole [5]. The molar volume of silicon tetraiodide, calculated from the data of reference [6], is 157.1 cc. Values of $(\Delta E_1/v_1)^{1/2}$ were taken from reference [7]. The value of $(\Delta E_2/v_2)^{1/2}$, calculated from vapor pressure data [6] is 9.07, which is somewhat lower than the value calculated from the solubility data.

The variations in the value of $(\Delta E_2/v_2)^{1/2}$ calculated for the various solutions are small, and chlorotoluene, and m-xylene fall in the series along with the other solvents in spite of their polarity. Taking into account the approximate data used in solving Equation (A), the agreement in the values of $(\Delta E_2/v_2)^{1/2}$ are very satisfactory. This shows that silicon tetraiodide actually forms regular solutions with the solvents studied.

LITERATURE CITED

[1] I.M. Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, 6, N. Y., 1925.

[2] B. Rubin, G. H. Moates I. R. Weiner, J. Electrochem. Soc., 104, 658 (1957).

[3] V. F. Alekseev, Mining J., No. 4, 83 (1879).

[4] J. H. Hildebrand, Chem. Rev., 44, 37 (1949).

[5] L. Quill, The Chemistry and Metallurgy of Miscellaneous Materials, N. Y., 1950.

[6] H. C. Andersen, L. H. Belz. J. Am. Chem. Soc., 75, 4828 (1953).

[7] J. H. Hildebrand, R. L. Scott, The Solubility of Nonelectrolytes, N. Y., 1950.

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SYNTHESIS OF AROMATIC COMPOUNDS OF GERMANIUM BY MEANS OF ARYLDIAZONIUM FLUOBORATES

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Aromatic compounds of tin and lead have been prepared through diazonium compounds by one of us together with K. A. Kocheshkov and co-workers[1]. Mainly diaryl derivatives are formed in the case of tin. When the double salts of stannic chloride with aryldiazonium chlorides are decomposed with powdered metallic tin, the best yields (23%) were obtained when Ar = C_6H_5. We obtained higher yields (up to 40%) of diaryldichlorostannanes [diaryltin dichlorides] by the decomposition of aryldiazonium fluoborates with the zinc dust in the presence of stannous chloride in acetone [2].

Better results were also obtained in the case of organolead compounds when aryldiazonium fluoborates in acetone were decomposed with powdered metallic lead [3] and also with a lead-sodium alloy [4]. In this way, tetraphenyllead was obtained in yields of 15% (decomposition with lead) to 30% (decomposition with the alloy), while tetraparatolyllead was obtained in 15% yield (decomposition with the alloy).

The present paper reports on the feasibility of using the diazo method for the synthesis of aromatic compounds of germanium. In contrast to $SnCl_4$ and $PbCl_4$, $GeCl_4$ does not form double salts with aryldiazonium chlorides. Aryldiazonium fluoborates were decomposed with metal powders in the presence of $GeCl_4$. The best of the metal reducing agents was zinc (zinc dust), and the best solvent was absolute acetone.

The reaction yielded monoarylated germanium compounds. Germanium compounds containing more than one aryl radical were not formed under these conditions.

The arylgermanium trichlorides were isolated and analyzed as the arylgermanonic acids. The latter were colorless, infusible powders. Anhydrides of arylgermanonic acids were prepared in which the aryl group was C_6H_5, p-$CH_3OC_6H_4$, P-$C_2H_5OC_6H_5$, p-BrC_6H_4, and p-ClC_6H_4. The anhydride of benzenegermanonic acid was obtained in a yield of 28% of theoretical; yields of the other anhydrides are given below.

Decomposition of benzenediazonium fluoborate in acetone in the presence of $GeCl_4$ and Zn dust. The reaction was carried out in a long, narrow beaker fitted with a Witt stirrer and a thermometer. 50 g of benzenediazonium fluoborate was introduced in small portions over a period of 20 minutes into a vigorously stirred suspension of 17.4 g of zinc dust in a solution of 25.15 g of $GeCl_4$ in 80 ml of dry acetone at −8°. With the addition of the first portions of diazonium salt, the temperature of the reaction mixture rose to 5°. The remainder of the diazonium salt was added at a rate such that the temperature did not rise above 5°. The stirring was continued for 5 hours, with cooling, after the addition of the diazonium salt. On the next day, 40 ml of dry acetone was added to the reaction mixture, and stirring was continued until the decomposition of the diazonium salt was complete (negative reaction with β-naphthol). The reaction mixture was treated with a 20% solution of NaOH. Over a period of 3 hours, the resulting precipitate was filtered and washed with acetone (Filtrate I). The major portion of the anhydride of benzenegermanonic acid was extracted from the precipitate by heating with a 20% solution of NaOH and subsequent acidification of the alkaline filtrates with concentrated HCl. After this treatment, the precipitate, which had been washed completely with acetone, alcohol, and ether, did not burn, which indicated the absence of $(C_6H_5)_2GeO$. Filtrate I separated into two layers: an acetone layer and an alkaline layer, from which an additional small amount of $(C_6H_5GeO)_2O$ was obtained by acidification. The acetone layer was combined with the acetone, alcohol, and ether filtrates from the washings, the solvents were evaporated in the cold, and the residue – a viscous oily mass – was treated several times with benzene. The benzene extracts

TABLE 1

Decomposition of ArN_2BF_4 in Acetone in the Presence of $GeCl_4$ and Zn Dust

Ar	ArN_2BF_4, g	Zn, g	$GeCl_4$, g	Acetone, ml	Temperature, °C		Amount of $(ArGeO)_2O$, g	Found, %		Calculated, %	
					Init.	Max.		C	H	C	H
p - $CH_3OC_6H_4$	28,7	8,65	16,6	75	—7	+6	0,23	40,71; 40,78	3,43; 3,59	41,26	3,46
p - $C_2H_5OC_6H_4$	25,1	7,0	15,0	80	—4	+5	0,17	44,38; 44,52	4,48; 4,52	44,12	4,16
p - ClC_6H_4	30,0	8,66	14,4	70	—7,5	—0,5	0,3	34,33; 34,17	2,09; 2,20	34,62	1,94
p - BrC_6H_4	67,0	16,17	26,9	80	—11	—5	1,0	29,43; 29,38	1,86; 1,81	28,53	1,59

were combined and washed with a 10% solution of NaOH (to extract possibly present GeO_2); the benzene was evaporated in the cold, and the residue was transferred to a quartz test tube where it was treated with a mixture of concentrated H_2SO_4 and HNO_3 to decompose all organic compounds. After boiling of the mixture for many hours, the excess acid evaporated, and the residue calcined, no GeO_2 was detected (the residue was extracted with alkali, and the solution, after the addition of an excess of concentrated HCl, was saturated with H_2S; GeS_2 did not precipitate), which indicates the absence of $[(C_6H_5)_3Ge]_2O$ and $(C_6H_5)_4Ge$ in the benzene extracts. The unreacted $GeCl_4$ was separated from the reaction mixture as GeS_2 by precipitation from the hydrochloric acid filtrates with H_2S.

5.58 g (27.3% of theoretical) of $(C_6H_5GeO)_2O$ was obtained. The material was purified by reprecipitation from a hot 10% solution of NaOH with HCl and subsequent washing with pyridine (1 time), water, alcohol, and ether.

Found %: C 41.21; 40.96; H 3.18; 3.08 $C_{12}H_{10}O_3Ge_2$.
Calculated %: C 41.5; H 2.90.

Data on the other arylgermanonic anhydrides, which were prepared under analogous conditions, are presented in Table 1.

LITERATURE CITED

[1] A. N. Nesmeianov, K. A. Kocheshkov and V. A. Klimova, J. Gen. Chem., 6, 176 (1936).

[2] A. N. Nesmeianov and L. G. Makarova, Proc. Acad. Sci. USSR, 87, 421 (1952).

[3] A. N. Nesmeianov, K. A. Kocheshkov and M. M. Nad', Bull. Acad. Sci. USSR, Div. Chem. Sci., 1945, 522.

[4] A. N. Nesmeianov and L. G. Makarova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, 380. *

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ALKYLGERMANIUM HYDRIDES AND ALKYLGERMANIUM DEUTERIDES

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(Presented by Academician A. A. Balandin, May 9, 1958)

From the time of Winkler's discovery of germanium in 1886 and his synthesis of the first germanium hydride ($HGeCl_3$) [1] down to the present time, a comparatively small number of inorganic and organic germanium hydrides have been prepared.* As regards germanium deuterides, the first member of this class of compounds** was prepared only in 1954; however, among those reported, not one is an organic germanium deuteride.

Moreover, the germanium hydrides and deuterides are of substantial interest from the point of view of the development of new methods for the preparation of organogermanium compounds and from the point of view of the study of the chemical and physical features of Ge–H and Ge–D bonds (as compared to C–H and C–D, Si–H and Si–D bonds as well as M–H and M–D bonds of the hydrides of various elements).

From the chemical point of view, it seemed of interest to study the possibility of broadly applying lithium hydride and deuteride to the synthesis of the indicated organogermanium compounds***, which, until our work, had not been studied.

From the point of view of the physical properties of Ge–H and Ge–D bonds, the change in the vibrational frequencies of these bonds with the accumulation of these bonds at a germanium atom was of interest to us.

Besides the above, it was necessary to determine, if only to a certain approximation, the refractions of the Ge–H and Ge–D bonds, data on which are not present in the literature.

The preparation and properties of the following organic germanium hydrides and deuterides are described in the present work:

1. $CH_3GeH_3 \rightarrow (CH_3)_2GeH_2 \rightarrow (CH_3)_3GeH$.
2. $CH_3GeD_3 \rightarrow (CH_3)_2GeD_2 \rightarrow (CH_3)_3GeD$.
3. $C_2H_5GeH_3 \rightarrow (C_2H_5)_2GeH_2 \rightarrow (CH_3)_2(C_2H_5)GeH$.
4. $C_2H_5GeD_3 \rightarrow (C_2H_5)_2GeD_2 \rightarrow (CH_3)_2(C_2H_5)GeD$.

All of these were prepared, in rather high yields, under the conditions used in the preparation of alkylsilane hydrides and deuterides [6] from the corresponding alkylgermanium chlorides (bromides), LiH, and LiD. The physical properties of the resulting compounds are presented in Table 1. It follows from the data of Table 1 that, on the average, the Ge–H bond refraction is about 3.38 ml/mole and the Ge–D bond fraction is 3.34 ml/mole.

As in the case of $(CH_3)_2GeCl_2$ and CH_3MgBr [8], during the preparation of the starting materials $(CH_3)_2(C_2H_5)GeCl$ and $(C_2H_5)_2GeCl_2$ by Grignard reaction using C_2H_5MgBr, the replacement of chlorine by bromine was observed. The yield of bromides was rather high under these conditions. All of these facts warrant the conclusion that chlorine atoms bonded to Ge have an increased ability (in comparison with analogous silicon compounds) to exchange with bromine under Grignard reaction conditions.

*At the present time, only 13 inorganic and 17 organic germanium hydrides are known, a large number of which have been described in the review of reference [2].

**GeD_4 [3], Ge_2D_6 [3], Ge_3D_8 [3], GeD_3H [4], GeD_3Cl [5], $GeDH_3$ [4].

***That it is feasible in principle to prepare germanium hydrides with the aid of $LiAlH_4$ was first demonstrated in 1947 by Finholt, Bond, Wilzbach and Schlesinger [7].

TABLE 1

Compound No.	Formula	B.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR found	Bond refract. in GeH and GeD
I	CH_3GeH_3	—23,5/745	—	—	—	—
II	CH_3GeD_3	—23,5/752	—	—	—	—
III	$(CH_3)_2GeH_2$	6,5/744	—	—	—	—
IV	$(CH_3)_2GeD_2$	6,5/745	—	—	—	—
V	$(CH_3)_3GeH$	26/755,5	1,0128	1,3890	27,72	3,36
VI	$(CH_3)_3GeD$	26/758,5	1,0207	1,3893	27,76	3,40
VII	$C_2H_5GeH_3$	11,5/743,5	—	—	—	—
VIII	$C_2H_5GeD_3$	11,3/748,5	—	—	—	—
IX	$(C_2H_5)_2GeH_2$	72,5/740,5	1,0378	1,4208	32,42	3,46
X	$(C_2H_5)_2GeD_2$	71,5/743,5	1,0525	1,4200	32,39	3,45
XI	$(CH_3)_2(C_2H_5)GeH$	62/755,5	1,0158	1,4090	32,31	3,32
XII	$(CH_3)_2(C_2H_5)GeD$	60/737,4	1,0262	1,4083	32,17	3,18

That it is possible for the Kharasch reaction to take place with germanium hydrides was shown by Fischer, West and Rochow [9] in 1954.

$$Cl_3Ge-H + CH_2=CHCH_2CH_2CH_3 \xrightarrow[62-64^\circ,35\ \text{hrs}]{Bz_2O_2} Cl_3GeCH_2CH_2CH_2CH_2CH_3.$$

$HGeCl_3$ and $(C_6H_5)_3GeH$ can add to a series of other unsaturated compounds in the presence of benzoyl peroxide [10,11].

By analogy with the silicon hydrides [12], in the present work, using trichlorogermane* and ethylene, we showed that it is possible to use as a catalyst for this reaction chloroplatinic acid, in the presence of which the reaction begins at room temperature and proceeds at a high rate.

In conclusion, we shall dwell for a moment on the Raman spectra of the alkylgermanium hydrides and deuterides considered above.

The literature contains data on the infrared absorption spectra of compounds of the type D_nGeH_{4-n} [13] as well as the Raman spectra of several other organogermanium compounds [14]. Both these data and data from the work of one of us [15], and also the Raman data given below for compounds VII-XII, permit the remarks which follow the Raman data:

1. $C_2H_5GeH_3$ (VII), ν (cm^{-1}): 170 (1), 239 (0), 347 (0), 522 (6), 616 (4), 780 (0), 828 (3), 882 (4 b), 974 (1), 1025 (1), 1220 (4), 1465 (0), 2062 (10), 2871 (6), 2917 (7s), 2925 (2), 2950 (2).
2. $C_2H_5GeD_3$ (VIII), ν (cm^{-1}): 161 (0), 232 (1), 425 (3), 583 (7), 600 (4), 632 (3), 683 (1), 799 (0), 818 (0), 965 (1), 1024 (1), 1103 (0), 1167 (1), 1221 (2), 1460 (0), 1475 (10), 2870 (7), 2915 (6 b), 2945 (2).
3. $(C_2H_5)_2GeH_2$ (IX), ν (cm^{-1}): 170 (1), 287 (2), 545 (5), 686 (0), 800 (0), 870 (3 b), 966 (1), 1023 (1), 1221 (4), 1422 (0), 1460 (1), 2032 (10), 2870 (9), 2909 (10), 2928 (4), 2946 (3).
4. $(C_2H_5)_2GeD_2$ (X), ν (cm^{-1}): 172 (1), 227 (0), 278 (3), 296 (0), 459 (0), 474 (4 b), 511 (4), 578 (8), 593 (4), 624 (3), 968 (3 b), 1023 (3 b), 1222 (7), 1401 (0), 1461 (10 b), 2870 (7), 2910 (8), 2927 (4s), 2948 (4 s).
5. $(CH_3)_2(C_2H_5)GeH$ (XI), ν (cm^{-1}): 164 (3), 185 (4), 286 (3), 554 (9), 586 (5), 624 (3), 847 (0), 969 (1), 1021 (1), 1106 (0), 1220 (3), 1240 (4), 1422 (1), 1468 (1), 2021 (5), 2871 (4) 2904 (8), 2925 (2), 2975 (3 b).
6. $(CH_3)_2(C_2H_5)GeD$ (XII), ν (cm^{-1}): 170 (1), 198 (1), 282 (2), 493 (4 b), 568 (10), 599 (6 b), 704 (0), 833 (0), 968 (1), 1024 (2), 1112 (2), 1220 (3), 1242 (4), 1405 (1), 1455 (7 b), 2870 (5), 2908 (8), 2915 (2), 2976 (3).

* $HGeCl_3$ with an admixture of $GeCl_4$ was used in the reaction.

From work on silicon hydrides and deuterides [6,16], it is known that an accumulation of H (or D) atoms at an Si atom in compounds of the type of R_nSiH_{4-n} or R_nSiD_{4-n} (R is an aliphatic radical) causes a successive increase in the vibrational frequencies of the Si–H and Si–D bonds.

A comparison of the spectral data presented above and the data of references [6, 16] shows changes of the same nature in the valence vibration frequencies of Ge–H and Ge–D, namely: ν(Ge–H) in the group ≡Ge–H is 2020 cm^{-1}, in =GeH_2 it is 2030 cm^{-1}, in –GeH_3 it is 2062 cm^{-1}, and in GeH_4 it is 2110 cm^{-1} (average value of the symmetrical and degenerate frequencies). For germanium deuterides, these values are, respectively: 1455, 1460, 1475, and 1513 cm^{-1} The difference between ν(Ge–D) and ν(Si–D) is that for germanium deuterides of the type –GeD_3 and=GeD_2 only one line is observed, while for silicon deuterides of the type –SiD_3 and= SiD_2 there are two. This could indicate further weakening of the interaction of Ge–D bonds with each other. Apparently, the changes in the frequencies of the valence vibrations of Ge–H and Ge–D, just as in the case of C–H, C–D, Si–H, and Si–D, can be connected not only with the mass, but also with the nature (evidently, chiefly the electronegativity) of the atoms and groups bonded to the central element.

From a consideration of these same spectra, it is also possible to establish, in accordance with references [13, 17], the characteristic frequencies of methyl and ethyl groups connected to Ge. For a methyl group, the deformation frequency is 1240 cm^{-1} and the valence vibration frequencies are ν(C–H) 2904 and 2975 cm^{-1}; for an ethyl group, these are, respectively, 1220 cm^{-1} * and ν(C–C), in the ethyl chain, 965 and 1024 cm^{-1}. Deformation frequencies of the type δ(H–Ge–H) and δ(D–Ge–D), according to the literature [13], are distributed in the regions of 900 and 600-650 cm^{-1}, respectively. In our case, the lines at 882 and 870 cm^{-1} relate to δ(H–Ge–H) respectively for (VII) and (IX), and two lines at 600 and 632 cm^{-1} (VIII) and 593 and 624 cm^{-1} (X) relate to δ(D–Ge–D).

EXPERIMENTAL

The reduction of the alkylgermanium chlorides (bromides) was carried out in the kettle of a fractionating column. The products were collected periodically, and were later redistilled in the same column. The LiH and LiD were carefully powdered prior to the experiments in a ball mill.

(I) was obtained in an amount of 4.5 g (50 % of theoretical) from 34 g of CH_3GeBr_3 (b.p. 168°) and 6 g of LiH in 50 ml of dioxane.

(II) was obtained in the amount of 4.9 g (52%) from 33 g of CH_3GeBr_3 and 7 g of LiD in 45 ml of dioxane.

(III) was obtained in the amount of 11.2 g (99%) from 28 g of $(CH_3)_2GeBr_2$ (b.p. 153°) and 4 g of LiH in 50 ml of dioxane.

(IV) was obtained in the amount of 7.1 g (67%) from 26 g of $(CH_3)_2GeBr_2$ and 4 g of LiD in 50 ml of dioxane.

(V) was obtained in the amount of 6.5 g (72%) from 11 g of $(CH_3)_3GeCl$ (b.p. 98°) and 3 g of LiH in 50 ml of dioxane.

(VI) was obtained in the amount of 4.5 g (70%) from 8 g of $(CH_3)_3GeCl$ and 3 g of LiD in 50 ml of dioxane.

(VII) was obtained in the amount of 5.6 g (54%) from 21 g of $C_2H_5GeCl_3$ (b.p. 141°) and 5 g of LiH in 50 ml of dioxane.

(VIII) was obtained in the amount of 6 g (56%) from 21 g of $C_2H_5GeCl_3$ and 7 g of LiD in 50 ml of dioxane.

(IX) was obtained in the amount of 7 g from 33 g of a mixture of $(C_2H_5)_2GeCl_2$ (b.p. 169°) and $(C_2H_5)_2GeBr_2$ (b.p. 201°) in 50 ml of dibutyl ether. The mixture of dichloride and dibromide used in the reaction was obtained by the reaction of 104 g of $C_2H_5GeCl_3$ with C_2H_5MgBr (60 g of C_2H_5Br and 12 g of Mg) in 500 ml of ether; the dichloride-dibromide mixture was distilled under vacuum in a column prior to use in the reduction.

Found %: C 36.13; 36.38; H 9.89; 9.21 $C_4H_{12}Ge$. Calculated %: C 36.19; H 9.11.

(X) was obtained in the amount of 10 g from 50 g of a mixture of $(C_2H_5)_2GeCl_2$ and $(C_2H_5)_2GeBr_2$ in 40 ml of dibutyl ether.

* 1228 cm^{-1} in chlorides [14].

Found %: C 36.35; 36.37; H + D 9.06; 9.17; Ge 53.88; 54.26 $C_4H_{10}D_2Ge$. Calculated %: C 35.65; H + D 10.47; Ge 53.88.

(XI) was obtained in the amount of 6 g from 39 g of a mixture of $(CH_3)_2Ge(Cl)(C_2H_5)$ (b.p. 125°) and $(CH_3)_2(C_2H_5)GeBr$ (B.p. 143°/755 mm, d^{20}_4 1.4952, $n^{20}D$ 1.4726) in 50 ml of dioxane.

Found %: C 36.26; 36.48; H 8.19; 8.99 $C_4H_{12}Ge$. Calculated %: C 36.19; H 9.11.

The dimethylethylgermanium chloride and bromide were obtained in the amount of 16 g each by the reaction of 180 g of $(CH_3)_2GeCl_2$ (two experiments) with C_2H_5MgBr in 1 liter of ether. After separation of the precipitate, the ether was distilled, and the residue was vacuum distilled in a column. Besides the products indicated above, $(CH_3)_2GeBr_2$ (36 g) was obtained; b.p. 153°/755 mm. Analysis showed that the $(CH_3)_2(C_2H_5)$ GeCl contained some of the original dimethyl-germanium dichloride. Analysis of the $(CH_3)_2(C_2H_5)GeBr$ gave the following results:

Found %: C 22.88; 22.71; H 5.15; 5.15; Br 37.43; 37.72; Ge 33.80; 33.74 $C_4H_{11}BrGe$. Calculated %: C 22.70; H 5.24; Br 37.76; Ge 34.30.

(XII) was obtained in the amount of 4 g from 42.9 g of a mixture of $(CH_3)_2(C_2H_5)GeCl$ and $(CH_3)(C_2H_5)$ GeBr and 6 g of LiD in 50 ml of dibutyl ether.

Found %: C 36.35; 36.45; H + D 9.37; 9.24; Ge 54.74 $C_4H_{11}DGe$. Calculated %: C 35.92; H + D 9.80; Ge 54.28.

$C_2H_5GeCl_3$ (XIII) was obtained in the following manner. 52.6 g of a mixture of $HGeCl_3$ and $GeCl_4$, obtained by the interaction of Ge with HCl at 700° and distillation under vacuum, and 1 ml of an 0.1 M solution of $H_2PtCl_3 \cdot 6H_2O$ in i-C_3H_7OH were charged to a 200-ml autoclave. While the ethylene (40 atm) was being fed, the reaction started slowly, and was accompanied by considerable evolution of heat (60-80°). A total of 35 atm of ethylene was absorbed. After distillation of the thickened reaction products under vacuum (78-80° at 110 mm Hg), distillation in a column gave: 1) 5.5 g of $GeCl_4$, b.p. 82°/763.5 mm; 2) 15 g of $C_2H_5GeCl_3$, b.p. 139°/763.5 mm, d^{20}_4 1.6006 $n^{20}D$ 1.4730.

The considerable amount of distillation residue (26 g) and the thickening of the products indicated possible decomposition of the $HGeCl_3$.

LITERATURE CITED

[1] C. Winkler, J. Prakt. Chem. (2) 34, 222 (1886).

[2] O. H. Johnston, Chem. Rev., 48, 259 (1951).

[3] A. H. Zeltmann, G. C. Fitzgibbon, J. Am. Chem. Soc., 76, 2021 (1954).

[4] L. P. Lindeman, M. K. Wilson, J. Chem. Phys., 22, 1723 (1954).

[5] R. C. Lord, C. M. Steese, J. Chem. Phys., 22, 542 (1954).

[6] V. A. Ponomarenko, Iu. P. Egorov and G. Ia. Vzenkova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1958, 54.*

[7] A. E. Finholt, A. C. Bond, K. E. Wilzbach, H. I. Schlesinger, J. Am. Chem. Soc., 69, 2692 (1947).

[8] V. A. Ponomarenko and G. Ia. Vzenkova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1957, 994.*

[9] A. K. Fischer, R. C. West, E. G. Rochow, J. Am. Chem. Soc., 76, 5878 (1954).

[10] R. Riemschneider, K. Menge, P. Klang, Az. Naturforsch., 116, 115 (1956).

[11] H. Gilman, C. W. Gerow, J. Am. Chem. Soc., 79, 342 (1957).

[12] V. A. Ponomarenko, V. G. Cherkaev, A. D. Petrov and N. A. Zadorozhnyi, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1958, 247.*

*Original Russian pagination. See C. B. Translation.

[13] L. P. Lindeman, M. K. Wilson, Z. Phys. Chem., 9, 29 (1956).

[14] E. R. Lippincott, P. Mercier, M. C. Tobin, J. Phys. Chem., 57, 939 (1953).

[15] Iu. P. Egorov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1957, 124.*

[16] A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov and Iu. P. Egorov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1957, 310. *

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HYDROGENATION OF SOME UNSYMMETRICAL DIARYLETHANES

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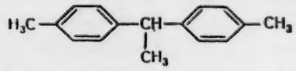
In the work reported in references [1-5], individual compounds – diarylethanes of the general formula Ar–CH(CH$_3$)–Ar or di(hydroxyaryl)-ethanes of the formula HO–Ar–CH(CH$_3$)–Ar–OH were obtained by alkylation of toluene, isopropylbenzene, diisopropylbenzene, phenol, cresol, and β-naphthol with acetylene in the presence of $H_3PO_4 \cdot BF_3$ catalyst.

We have now hydrogenated these compounds in a Musaev-Gal'pern apparatus under elevated temperatures and pressures using commercial Ni-on-kieselguhr catalyst.

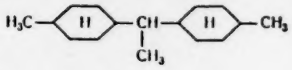
Hydrogenation of Ethylideneditolyl (EDT) [1,1-Di(p-tolyl)ethane]



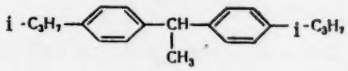
20 g of EDT and 5 g of catalyst were charged to the autoclave; the temperature was 250-300°, and the pressure was 100-150 atm.

After 8 hours, the product was removed from the autoclave, filtered, washed with alkali and with water, dried with calcium chloride, and distilled under vacuum. A clear, oily liquid was obtained; b.p. 108-110°/2mm, d^{20}_4 0.8502, $n^{20}D$ 1.4800. Mol. wt.: found, 216, calculated for $C_{16}H_{30}$, 222. MR_D found 72.8; calculated 71.7

The compound was identified as 1,1-(4,4'-dimethyl)dicyclohexyl-ethane

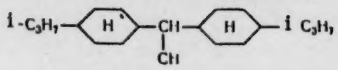


Hydrogenation of Ethylidenediisopropylbenzene [1,1-Di(p-cumenyl)ethane]

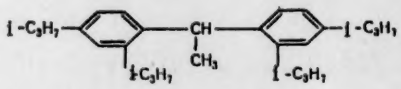


This experiment was carried out under conditions analogous to those used in the hydrogenation of EDT. The product was an oily, transparent liquid; b.p. 160-162°/4 mm, d^{20}_4 0.8989, $n^{20}D$ 1.4898. The viscosity was 20.4 centistokes at 50° and 3.9 centistokes at 100°. Mol. wt.: found, 275 and 279; calculated for $C_{20}H_{38}$, 278. MR_D found, 90.0; calculated, 90.2.

The compound was identified as 1,1-(4,4'-diisopropyl)dicyclohexylethane

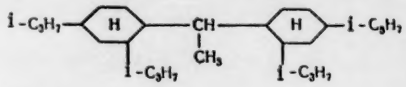


Hydrogenation of Ethylidenediisopropylbenzene [1,1-Di(2,4-diisopropylphenyl) ethane]

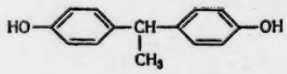


The product obtained by hydrogenation of the above compound under conditions similar to the preceding. The product was a transparent, viscous liquid; b.p. 177-179° / 1 mm, $n^{20}D$ 1.4980. Mol. wt.: found, 356; calculated for $C_{26}H_{50}$, 362.

The compound was identified as 1,1-(2,2',4,4'-tetraisopropyl)-dicyclohexylethane

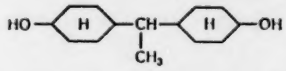


Hydrogenation of Phenol Alkylate

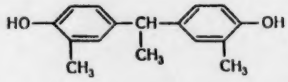


The hydrogenation was carried out at a temperature of 280° and a pressure of 100 atm ; the nickel-on-kieselguhr catalyst amounted to 20% of the alkylate; the solvent was n-heptane. The hydrogenation was continued for 10 hours until the formolite reaction gave a negative test. The purified product — the hydrogenizate — was a transparent, viscous liquid; $n^{20}D$ 1.5065, d^{20}_4 1.007, b.p. 160-165° / 6 mm. Mol. wt.: found, 236 and 232; calculated for $C_{14}H_{26}O_2$, 226.

MR_D found, 66.5; calculated, 65.5. The compound was identified as 1,1-(4,4'-dihydroxy)dicyclohexylethane.

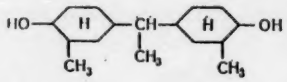


Hydrogenation of Ethylidene-o-cresol [1,1-Di(4-hydroxy-3-methylphenyl)ethane]



The hydrogenation was carried out as in the hydrogenation of the phenol alkylate. A transparent, viscous liquid was obtained. B.p. 160-165° / 3 mm, $n^{20}D$ 1.4815, d^{20}_4 0.9620. Mol. wt.: found, 260; calculated for $C_{16}H_{30}O_2$ 254. MR_D found, 75.5; calculated, 74.8.

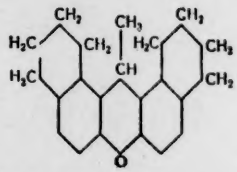
The compound was identified as 1,1-(4,4'-dihydroxy-3,3'-dimethyl)-dicyclohexylethane



Hydrogenation of β-naphthol alkylate

The hydrogenation was carried out under conditions analogous to the preceding. A transparent, viscous liquid was obtained. B.p. 178-179°/1 mm, $n^{20}D$ 1.5151, d^{20}_4 0.9800. Mol. wt.: found, 308 and 302; calculated for $C_{22}H_{24}O$, 304. MR_D found 92.5; calculated, 91.6.

This hydrogenated compound was identified as di(tetrahydronaphtho)pyran:



These hydrogenated compounds, which have been prepared for the first time, can serve as a basis for a deep theoretical and practical study of the hydrogenation of diarylethanes.

LITERATURE CITED

[1] V. L. Vaiser, Proc. Acad. Sci. USSR, 87, No. 4 (1952).

[2] V. L. Vaiser, and A. M. Polikarpova, Proc. Acad. Sci. USSR, 84, No. 1 (1952).

[3] V. L. Vaiser, Proc. Acad. Sci. USSR, 103, No. 5 (1955).

[4] V. L. Vaiser and A. M. Polikarpova, Proc. Acad. Sci. USSR, 108, No. 3 (1956).*

[5] V. L. Vaiser, Proc. Acad. Sci. USSR, 115, No. 1 (1957).*

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CATALYTIC CURING OF POLYDIMETHYLSILOXANE AT ROOM TEMPERATURE

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(Presented by Academician A. V. Topchiev, April 28, 1958)

As is well known, the process of converting linear or branched polyalkylsiloxanes to an infusible and insoluble state proceeds at 200-250° and requires a long time. The necessity of such a thermal treatment complicates the technological production of materials based on organosilicon polymers, and, to a significant extent, it limits the field of application of these polymers.

In spite of the importance of the problem of curing liquid and rubbery organosilicon polymers at room temperature, a means for the solution of this problem has not been proposed up to the present time. Only brief reports of an advertising nature have appeared in the literature, these indicating that in the USA a cold-curing organosilicon rubber has been developed (RTV Silastic) [1,2]. We considered it possible that three-dimensional polyalkylsiloxanes could be formed through the use of the interaction of the hydroxyl groups of linear polydimethylsiloxanes with the alkoxy groups of polyfunctional organosilicon monomers.

Such a method of forming cross-linking siloxane bonds is more favorable from an energy point of view than the splitting of hydrogen or an alkyl radical from a polymer chain, which is the basic principle of ordinary thermal vulcanization of polydimethylsiloxane rubber, and such a method can, therefore, be used at significantly lower temperatures.

As one of the objectives of a search for effective vulcanization accelerators, we carried out an investigation of the catalytic activity of certain esters of orthotitanic acid (ethyl, propyl, and butyl) and also of a number of organotin compounds, a large part of which belonged to the group of dialkyltin salts with the general formula $R_2Sn(OCOR_1)_2$, where R is an ethyl or butyl radical and $OCOR_1$ is acetyl, capryl, or stearyl.

The caprylates and stearates were synthesized for the first time, but the former were not individual compounds, since they were prepared from a fraction of technical caprylic acid.

In all cases, cold vulcanization of liquid and rubbery polydimethylsiloxanes took place, as shown by the gradual increase in viscosity and shear stress of the polymer, by an increase in its elasticity, and by a decrease in solubility. In Figues 1 and 2 are presented curves characterizing the change in shear stress (Π) and elasticity (recovery) of the polymer under the influence of organotitanium compounds, and certain properties of the vulcanizates are presented in Table 1.

For measuring the shear stress and elasticity of the polymers, we used a laboratory apparatus – a torsion plastometer – specially developed for the characterization of the plastic properties of organosilicon rubber [4]. The resulting data show that the nature of the vulcanization process changes sharply depending on the type of organometallic compound used. The esters of orthotitanic acid caused a rapid change in the properties of the polymer in the initial stage of the reaction, after which the rate of the process decreased sharply; the resulting polymer, as seen from the data of Table 1, had low shear stresss values and an increase in the content of soluble fraction.

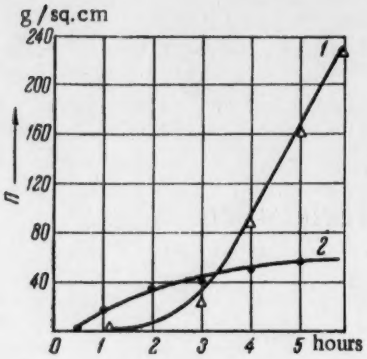


Fig. 1. Change in shear stress during vulcanization of an organosilicon polymer under the influence of: 1) an organotin compound (0.7%), 2) butyl titanate (3%).

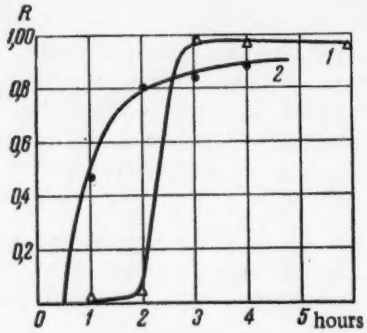


Fig. 2. Change in the elastic properties (recovery) during vulcanization of an organosilicon polymer under the influence of: 1) an organotin compound (0.7%), 2) butyl titanate (3%).

TABLE 1

Properties of Vulcanizates Cured at 20° (for 24 hours)

Vulcanization accelerator	Amount of accelerator, %	Shear stress, g/sq.cm.	Elasticity	Content of soluble fraction, %
Butyl titanate	3.0	190	0.95	31.5
Organotin compound	0.7	560	1.00	27.8

It should be noted that the esters of orthotitanic acid, in contrast to the organotin compounds, were able to promote vulcanization of the polydimethylsiloxanes in the absence of tetraethoxysilane; the latter merely promoted somewhat more complete vulcanization without changing its nature. This fact indicates that the esters of orthotitanic acid are not catalysts, but components of the vulcanization reaction of polydimethylsiloxanes directly participating in the formation of the cross links. In our opinion, this also explains the peculiarity of the curve presented in Figure 1, characterizing the vulcanization process; the high initial reaction rate is connected with the vigorous development of branching and cross-linking processes of the macromolecules of polydimethylsiloxane as a result of their interaction with hydroxyl groups formed by the hydrolysis of the ester of orthotitanic acid, and the subsequent retardation of the reaction is a natural consequence of the decrease in the mobility of the macromolecule with an increase in the amount of cross-linking bonds.

The cross-linking process promoted by the organotin compounds is of a totally different character. A characteristic of it is the presence of a specific induction period, which is replaced by a period of sharp increase in reaction rate during which the vulcanization process is practically completed. The duration of the induction period and the rate of the vulcanization process depend, as our experiments showed, on the nature and amount of the catalyst and also on the molecular weight of the polymer.

In Figure 3 are presented curves showing the change in shear stress of liquid polydimethylsiloxanes; these curves show that, with a decrease in the molecular weight of the polymer, the reaction rate decreases but the induction period increases. The mechanical properties of the vulcanizates were practically independent of molecular weight, as in shown by the investigation of the strength and specific elongation of reinforced vulcanizates (rubber) in the molecular-weight range of from 40,000 to 100,000; however, with the transition to high polymer of the type SKT synthetic rubber (molecular weight 300,000 to 500,000) there is observed a considerable increase in strength The following data are presented by way of example:

Polymer molecular weight	Yield strength of vulcanizate kg/sq. cm.	Elongation, %
70,000	21.8	180
400,000	37.6	350

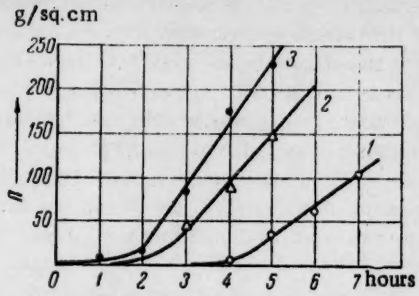
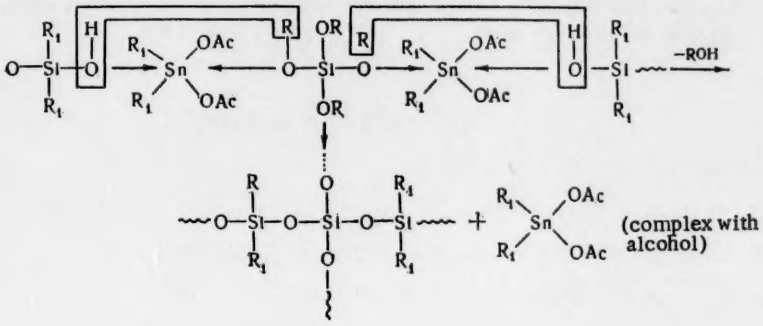


Fig. 3. Variation in vulcanization rate with polymer molecular weight, 1) 48,000 mol. wt.; 2) 63,000 mol. wt.; 3) 77,000 mol wt.

Interesting data were obtained during the investigation of the effect of the structure of the organotin compounds on their catalytic activity. In Figure 4 are presented the results of a series of experiments on the determination of the change in shear stress of a polydimethylsiloxane (60,000 molecular weight) in the presence of organotin compounds at equimolar dosage levels; these organotin compounds differed in the nature of the alkyl and acyl radicals entering into their composition.*

If we compare in Figure 4 the curves relating to dialkyl derivatives with the same alkyl groups (for example, 1, 2, and 3 or 4 and 5) and the curves corresponding to organotin compounds with the same acyl groups but with different alkyl groups (for example, 2 and 4 or 3 and 5), it is possible to conclude that with an increase in the size of the organic radicals entering into the composition of the stannates, their catalytic activity decreases, as shown by the increase in the induction period and the decrease in rate. It was very interesting that an increase in the size of the alkyl radical caused a more significant decrease in catalyst activity than did an increase in the size of the acyl group (as may be seen, for example, by comparing Curves 1 and 2 with 4 and 2).

These regularities, and also the mechanism of the catalytic action of the organotin compounds, can, in our opinion, be explained on the basis of the assumption of the formation of an active complex according to the scheme presented below.



The larger the alkyl radical, the greater the degree of saturation of the tin with electrons, the less the OH and OR groups are polarized, and, consequently, the more difficultly they react with each other. This same reasoning relates, to a lesser estent, to the effect of the acyl groups. However, as a consequence of the shifting of π-electrons to the oxygen, the positive induction effect, caused by the increase in the size of the alkyl radical, will appear to a lesser extent. As may be seen, the proposed mechanism is completely confirmed by the experimental facts, and it provides a basis for establishing a connection between the structure of the catalyst and its activity. Just after our work was concluded, there appeared a brief communication on the vulcanization of polydimethylsiloxane using dibutyltin aurate and tetraethoxysilane [4]; in this report, opinions analogous to ours on the role of tetraethoxysilane in the vulcanization process were expressed, but no explanation of the mechanism of the action of the catalysts was given.

This method of "cold" vulcanization of liquid and rubbery polydimethylsiloxane polymers can be used for the production of various rubbery materials, cast compositions, rubber-coated cloth, coverings, and compounds, which are cured at room temperature.

* The curve corresponding to diethyltin diacetate could not be obtained under the conditions of the present experiment, since, in view of the extremely high activity of this catalyst, its introduction into the polymer caused structure formation and partial vulcanization of the polydimethylsiloxane.

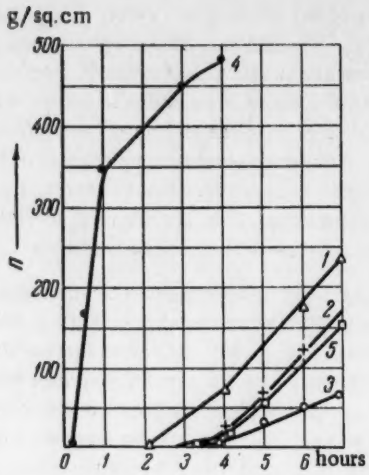


Fig. 4. Effect of the nature of the catalyst on vulcanization rate. 1) Dibutyltin diacetate, 2) dibutyltin dicaprylate, 3) dibutyltin distearate, 4) diethyltin dicaprylate 5) diethyltin distearate.

The organosilicon rubbers obtained by this method have 1½ to 2 times more strength than do rubbers of the same composition obtained by the usual two-stage vulcanization process at 150-200° in the presence of benzoyl peroxide. In Table 2 are presented comparative data on two rubbers reinforced with zinc oxide and prepared by the "cold" and "hot" vulcanization methods. Depending on the composition of the catalyst, the vulcanization time can be varied from several minutes to several days. These rubbers have good thermal stability – they retain their elasticity and mechanical strength over a long period under the influence of a temperature of 200-250°.

TABLE 2

Mechanical Properties of Organosilicon Rubbers Obtained by Different Methods

Vulcanizing agent	Vulcanization conditions		Tensile strength, kg/sq. cm.	Elongation, %	Shore hardness
	Temp., °C	Time hrs			
Benzoyl peroxide	150	0.5	20–25	180–250	40–50
" "	200	12			
Organotin compound	20	24	35–47	250–350	45–55

The authors express their appreciation to E. N. Zil'berman and N. A. Rybakova for the synthesis of the butyl-substituted organotin compounds, and to O. V. Nogina for the gift of the samples of the esters of orthotitanic acid used in the present work.

LITERATURE CITED

[1] Materials and Methods, 39, 5, 233 (1954).

[2] Ind. Rub. World, 130, 11, 112 (1954).

[3] Iu. B. Dubinker and V. P. D'iakonova, Factory Labs., 10, 1262 (1952).

[4] S. Nitzsche and M. Wick-Kunststoffe, 47, 8, 431 (1957).

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A NEW METHOD OF SYNTHESIS OF TRIS(TRIALKYL(ARYL)SILYL) BORATES

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(Presented by Academician A. V. Topchiev, May 30, 1958)

Up to now, only fragmentary information on the preparation of organosilicon esters of boric acid has been available in the literature [1-4].

The present work is a continuation of our studies on the dehydrocondensation of trialkyl(aryl)silanes with organic molecules containing hydroxy, oxo, or polyhydric groups.

We have previously pointed out [5, 6] that trialkyl(aryl)silanes smoothly react with hydroxy, carboxy, and polyhydric organic compounds in the presence of nonalkyline catalysts.

We have found that trialkyl(aryl) silanes undergo dehydrocondensation with boric acid in the presence of a small amount, 0.01-1% (of the trialkyl (aryl)-silane), of an anhydrous halide of cobalt, nickel, palladium, or platinum; no by-products are formed, and the yield of the corresponding tris(trialkyl(aryl)silyl) borate reaches 90-95% of theoretical.

The reaction is carried out by heating a mixture of the reactants, and it is readily controlled by the rate and amount of evolved hydrogen. The process proceeds according to the simplified scheme:

$$3R_3SiH + (OH)_3B \rightarrow (R_3SiO)_3B + 3H_2.$$

The tris(trialkyl(aryl)silyl) borates prepared by this method are distinguished by their high purity, and they are colorless liquids with a characteristic odor; they may be distilled without decomposition. They are readily hydrolyzed by water and by dilute alkalies and acids.

The physical constants, yields, and analytical data for the tris(trialkyl(aryl)silyl) borates prepared by us are presented in Table 1.

TABLE 1

Tris(trialkyl(aryl)silyl) Borates

$(R_3SiO)_3B$ R_3Si—	B. p. °C/mm Hg	d_4^{20}	n_D^{20}	B, %		Si, %		Reaction time, min	Yield, %
				Calc	Found	Calc.	Found		
$(C_2H_5)_3$ Si—*	195/9,5	0,8921	1,4380	2,68	2,67:2,65	20,83	20,88:21,00	480	94,1
$(n\text{-}C_3H_7)_3Si$—	215—217/1	0,8662	1,4425	2,04	2,08:2,00	15,87	15,60:15,68	52	90,6
$(n\text{-}C_4H_9)_3Si$—	273—274/3	0,8753	1,4488	1,65	1,62:1,69	12,82	12,73:12,85	55	88,7
$CH_3(n\text{-}C_3H_7)_2Si$—**	185/3	0,8661	1,4308	2,42	2,40:24,5	18,86	18,68:18,90	45	95,5
$CH_3(n\text{-}C_4H_9)_2Si$—	232/4	0,8736	1,4370	2,04	2,01:2,09	15,87	15,70:15,86	210	89,8
$CH_3(n\text{-}C_5H_{11})_2Si$—	273—274/9	0,8613	1,4410	1,76	1,74:1,79	13,70	13,59:13,36	42	94,2
$C_2H_5(n\text{-}C_3H_7)_2Si$—	214/3	0,8768	1,4410	2,21	2,23:2,30	17,24	16,20:16,77	180	96,7
$C_2H_5(n\text{-}C_4H_9)_2Si$—	235/3	0,8875	1,4462	1,89	1,91:1,96	14,70	14,75:15,21	219	95,3
$C_2H_5(i\text{-}C_5H_{11})_2Si$—	297—298/11	0,8753	1,4480	1,65	1,72:1,62	12,82	12,82:12,74	47	95,1
$C_2H_5(C_6H_5)_2Si$—***	354—358/8	1,086	1,5796*	1,56	1,60:1,57	12,16	12,17:12,13	147	92,5

* Literature data . . . . (4): b. p. . 178 — 179°/13 mm d_4^{20} 0,8918; n_D^{20} 1,4382.

** Literature data . . . . (4): b. p. 157—160°/1 mm d_4^{20} 0,8668; n_D^{20} 1,4332.

*** At 50° (viscous liquid).

EXPERIMENTAL

Starting materials. The trialkyl(aryl)silanes were prepared by reacting trichlorosilane, methyldichlorosilane, or ethyldichlorosilane with the appropriate alkylmagnesium halides; they were purified in a column (under vacuum for the high-boiling compounds).

The boric acid – a chemically pure preparation – was ground to a fine powder, and dried over calcium chloride.

The halides of cobalt, nickel, palladium, and platinum – pure preparations – were carefully dehydrated by the usual method [7].

Analysis. The boron in the tris(trialkyl(aryl)silyl)borates was determined in the form of boric acid by titration of a weighed sample with an 0.2 N solution of KOH (thymol blue indicator); the titration was carried out in an aqueous-alcoholic medium in the presence of mannitol. The titer of the solution of base was determined with an aqueous-alcoholic solution of pure boric acid of the same concentration, the boric anhydride content of which had previously been determined (gravimetric method).

Silicon was determined by difference from the total silicon and boron oxides formed by treatment of a weighed sample of the substance with a mixture of oleum and concentrated nitric acid with subsequent calcination of the oxides at a temperature of 900-950° [4].

Typical synthesis of tris(ethyldiisoamylsilyl)borate. A mixture of 34 g (0.17 mole) of ethyldiisoamylsilane, 3.1 g (0.05 mole) of orthoboric acid, and 0.1 g (0.0077 mole) of anhydrous nickel chloride was heated at a temperature of 110-120° until hydrogen evolution ceased completely (47 minutes). Distillation of the reaction mixture gave 31.3 g of tris(ethyldiisoamylsilyl) borate with a b.p. of 296-300°/11 mm; the yield was 95% of theoretical. After a second distillation, the tris(ethyldiisoamylsilyl) borate had a m.p. of 297-298°/11 mm; d^{20}_4 0.8757; $n^{20}D$ 1.4480.

Found %: B 1.72; 1.62; Si 12.82; 12.74. $C_{36}H_{81}Si_3O_3B$. Calculated %: B 1.65; Si 12.82.

Synthesis of the other tris(trialkyl(aryl)silyl) borates was carried out analogously at a temperature of 100-130° and a mole ratio of reagents, $R_3SiH/B(OH)_3/MX$, of 0.17/0.05/0.0077.

LITERATURE CITED

[1] U.S. Patent 2440101 (1948).

[2] E. Wiberg, U. Krüerke, Z.. Naturforsch., 8b, 609 (1953).

[3] F. Henglein, R. Lang, K. Scheinost, Makromol. Chem., 15, 177 (1955); Chimia, 9, 187 (1955).

[4] M. G. Voronkov and V. N. Zgonnik, J. Gen. Chem., 27, 1476 (1957).*

[5] B. N. Dolgov, Iu. I. Khudobin and N. P. Kharitonov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1958, 113.*

[6] B. N. Dolgov, N. P. Kharitonov, N. E. Glushkova and Iu. I. Khudobin, J. Gen. Chem., 28, No. 10 (1958).*

[7] Iu. V. Kariakin and I. I. Angelov, Pure Chemical Reagents, Moscow, 1955.**

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ON THE PREPARATION OF GRAFT COPOLYMERS OF POLYAMIDES WITH VINYL MONOMERS

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Graft copolymers have recently more and more begun to attract the attention of investigators owing to the new synthesis routes which have been discovered. Immergut and Mark [1] have published a review article on the preparation of graft and block copolymers by various methods. All of the proposed methods are adequate, but they are applicable only for grafting to polymers which are in solution; an exception is a method developed by Chapiro [2], which is based on the preliminary action of penetrating radiation on the polymer leading to cleavage of the molecule and the formation of free macroradicals. In the majoritv of cases, there is simultaneous formation of graft and block copolymers with all of these methods.

We undertook to develop a method for the preparation of graft copolymers which would not lead to the simultaneous formation of block copolymers. With this goal, the original polyamides were first subjected to the action of ozone, and were then treated with the vinyl monomers – styrene or methylmethacrylate. This procedure resulted in the formation of a layer of graft copolymer on the surface of the polyamide.

First, we examined the effect of ozone on polyamides. For this purpose, caprone [nylon] films were subjected to the action of ozone for different lengths of time from 2 minutes to 6 hours, and their properties were then determined.

The results of these tests are presented in Table 1.

TABLE 1

Change in the Mechanical Properties of Caprone [Nylon] Samples After Ozonation and Polymerization with Styrene (average of 4 experiments)

Original sample of caprone		Ozonation time	Same sample after ozonation		Same sample after ozon. and polym. with styrene (5 hr. / 80°)	
E	σ		E	σ	E	σ
733	779	2 min	726	798	741	818
733	779	5 min	774	856	740	814
824	728	10 min	849	738	902	693
718	870	20 min	787	864	858	714
718	870	1 hr	570	682	601	658
718	870	3 hrs	686	544	672	603
824	728	6 hrs	667	571	556	525

Note. Here and in Table 2: E is elongation at break (%), σ is tensile strength (kg/sq. cm.).

* A.P. Zasechkina participated in the experimental work.

As may be seen from Table 1, with a change in ozonation time, the properties of the caprone film change so that both the tensile strength and the elongation at break drop. However, with short ozonation times of 10-20 minutes there is practically no deterioration in the properties of the films; on the contrary, there is even an increase in mechanical strength, and only with an increase in ozonation time to 1 hour is there a drop in strength.

It is interesting to note that if the samples are heated for some time (5 hours) after ozonation, the properties of the polymer change appreciably — tensile strength and elongation decrease. After ozonation, the films acquire the ability to liberate iodine from a solution of potassium iodide, which indicates the presence of an oxidizing agent in the films.

After ozonation, the films were placed in styrene, and were kept in the liquid monomer for 5 hours at 80° in an atmosphere of nitrogen. The films were then washed in boiling benzene for 1 hour, and then were rinsed in cold benzene.

The films so-treated were subjected to mechanical tests, from which it became clear that their mechanical strength was usually somewhat higher than that of the original films when the ozonation time was brief, and was very little changed from the strength of the films after ozonation, as may be seen from Table 1. The maximum change in weight during polymerization did not exceed 20%.

We also carried out similar experiments with films prepared from anide G-669, a polyamide copolymer obtained from E-caprolactam, hexamethylenediamine adipic acid amide, and hexamethylenediamine azelaic acid amide [3]. The results of these experiments are presented in Table 2.

TABLE 2

Change in the Mechanical Properties of Anide G-669 After Ozonation and Polymerization with Styrene (average of 4 experiments)

Original sample of anide G-669		Ozonation time *	Same sample after ozonation		Same sample after ozon. and polym. with styrene (5 hours at 80°)	
E	σ		E	σ	E	σ
685	485	2 min	768	472	648	470
454	400	10 min	547	389	570	392
454	400	12 min	534	425	651	425
454	400	15 min	753	496	328	383
669	554	4 hrs **	608	587	657	482
669	554	4 hrs ***	676	564	675	554
454	400	6 hrs	409	411	225	301

*Oxygen flow rate 80-85 ml/minute.
**Maximum rate (140 ml/minute).
***Minimum rate (40 ml/minute).

As may be seen from Table 2, the picture was the same in this case as in the case of polycaprolactam.

In addition, we measured the specific viscosity both of the original samples of polyamides and of these same samples after ozonation and polymerization. The results are presented in Table 3.

As may be seen, there was an increase in the specific viscosity of the solution after polymerization of the ozonized sample of polyamide.

In Table 4 are presented the elemental analyses of several of the graft copolymers.

TABLE 3

Change in the Specific Viscosity (η_{sp}) of Samples of Polyamides After Ozonation and Polymerization (average of 4 experiments)

Film	Before ozonation	After a 2-minute ozonation	After polymerization	After a 5-minute ozonation	After polymerization	After a 3-hour ozonation	After polymerization	After a 5 hour ozonation	After polymerization
Caprone	0,538	0,599	0,712	0,704	0,740	0,739	0,785	0,622	0,491
Anide G-669	0,465	—	—	0,549	0,635	—	—	0,637	0,771

TABLE 4

Change in Elemental Composition of Samples of Polyamides After Ozonation and Polymerization

Film	Before ozonation		After a 5-minute ozonation %	After polymerization, %	Wt. increase, % of orig. (av.)	After a 5-hour ozonation, %	After polymerization, %	Wt. increase % of orig. (av.)
	Calc. %	Found %						
Caprone	C 63,11 H 10,60 N 12,27	C 64,03 H 9,64 N 12,18	C 63,32 H 9,80 N 12,44	C 63,98 H 9,64 N 12,18	12,5	C 63,44 H 9,64 N 11,83	C 69,93 H 9,14 N 9,77	18,5
Anide G-669	C 64,96 H 10,06 N 11,65	C 63,91 H 9,68 N 11,16	C 64,53 H 9,90 N 12,09	C 65,63 H 9,75 N 11,05	8,3	C 64,26 H 9,97 N 11,57	C 70,86 H 9,47 N 9,56	21,12

Experiments were also carried out in which methyl methacrylate was grafted to the polyamides; the corresponding graft copolymers were obtained.

On the basis of the data obtained, it can be concluded that as a result of our procedure, a layer of polystyrene or of methyl methacrylate polymer was formed: this layer was apparently formed on the surface of the film or fiber of polyamide, and was bound to it by chemical bonds. In this case, obviously, the formation of a molecule of graft copolymer took place in the surface layer of the polyamide; the grafted layer did not increase without limit – it did not exceed 20%. Concurrently, there was a change in the surface properties of the polyamide, which found expression in a decline in the wettability of the films by alcohol. The grafted polyamide anide G-669 lost its ability to dissolve completely in alcohol. The solubility in cresol and formamide also changed somewhat.

It is possible to believe that the reaction proceeds as follows:

$$-(CH_2)_n-CONH-(CH_2)_n- \xrightarrow{O_2} -(CH_2)_n-CO-\underset{\underset{OOH}{|}}{N}-(CH_2)_n- \xrightarrow{RCH=CH_2}$$

$$\longrightarrow -(CH_2)_n-CO-\underset{\underset{OCH_2-\underset{\underset{R}{|}}{CH}-}{|}}{N}-(CH_2)_n-$$

Obviously, the formation of peroxide compounds at the amide groups of the polyamide proceeds first, and molecules of the vinyl monomer then add at these peroxide groups.

LITERATURE CITED

[1] E. H. Immergut, H. Mark, Makromol. Chem., 18, 19, 322 (1956).

[2] A. Chapiro, J. Polym. Sci., 29, 321 (1958).

[3] V. V. Korshak and T. M. Frunze, Proc. Acad. Sci. USSR, 97, 675 (1954).

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ON SOLUTIONS OF SILICIC ACID IN ACETONE

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The literature contains only isolated indications of the possibility of extracting silicic acid with polar organic compounds [1, 2]. This process is based on the formation of complexes of silicic acid with organic compounds of a specific type. There are no data in the literature on the feasibility of extracting silicic acid from aqueous solutions with acetone.

In connection with the technical problems involved in the search for a route for the preparation of sufficiently stable and concentrated solutions of silicic acid, which can be used as a bonding material in the preparation of refractory linings used in the production of castings by means of fusible models, the possibility of preparing solutions of silicic acid in acetone and the properties of such solutions were studied. Acetone was selected as being the most available organic solvent with a sufficiently high volatility.

The starting material for the preparation of the acetone solution of silicic acid was water glass. After neutralization with sulfuric acid carried out so that the acidity was 0.1-0.2 N and the temperature did not exceed 18°, the solution was agitated with an equal volume of acetone, and table salt was added to bring about separation into layers. After stratification, the acetone layer could be separated from the water layer.

The resulting acetone solution contained 11-12 wt.% SiO_2. The silicic acid content of the acetone solution depended chiefly on the volume of acetone used in the extraction. The silicic acid content of the acetone solution could be increased to 18-19% SiO_2 by decreasing the volume of acetone. The stability of these acetone solutions decreased with an increase in the concentration of silicic acid; gel formation occurred when the solutions were allowed to stand. Solutions with a content of up to 12% could be stored for several months without visible change, while in solutions containing 18-19% SiO_2, gel appeared after 2 weeks. The density of the acetone solutions increased with an increase in the concentration of silicic acid, and it exceeded 1.0 in 18-19% solutions; however, no direct proportionality was found between the density of the solution and the silicic acid content.

Acetone extracts silicic acid in various degrees of polymerization. Polymerization of the silicic acid continues in the acetone solution itself. It was natural to assume that the less polymerized the silicic acid in the aqueous solution prior to extraction, the more stable would be the acetone solution. An experiment completely confirmed this assumption. The rate of polymerization of silicic acid in aqueous solutions is lowest at a pH of 1-2; this circumstance dictated the selection of the acidity of the neutralized solution.

Experiment showed that the contact time of the aqueous solution of silicic acid with acetone has a substantial significance in the preparation of a stable acetone solution of silicic acid; 3-5 minutes mechanical stirring of the aqueous solution with the acetone is required for the preparation of stable solutions. A further increase in the extraction time leads to only a small increase in the concentration of silicic acid and, moreover, to a decrease in the stability of the solution. Acetone solutions of silicic acid have a substantial practical significance. The nature of these solutions is still insuficiently clear, and it merits a more detailed study.

LITERATURE CITED

[1] R. Iler, P. Pinkey, Ind. and Eng. Chem. 11, 1379 (1947).

[2] R. Iler, J. Phys. Chem. 56, 6, 673 (1952).

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SYNTHESIS OF AROMATIC ORGANOMETALLIC COMPOUNDS OF BISMUTH THROUGH DIAZO COMPOUNDS

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Up to the present, the synthesis of oraganometallic compounds by the decomposition of double salts of diazonium compounds by means of metal powders (the method of double salts of diazonium compounds), a method which was proposed by one of us [1], has been used for the preparation of compounds of the following metals: Hg [1], Tl [2], Sn [3], Pb [4], Sb [5], and Bi [6-9]. It has also been shown that higher yields of Pb [10, 11], Sn [12], and Tl [2] organometallic compounds are obtained by the decomposition of aryldiazonium fluoborates rather than double salts of diazonium compounds with a halide of the metal. The results of the synthesis of organobismuth compounds by the decomposition with copper [6], zinc dust, or metallic bismuth [7-9] of double salts of bismuth trichloride with diazonium chlorides were not always satisfactory.

Through a systematic investigation of the decomposition of diarylbromonium fluoborates by metal powders, we established a close analogy between the results of these reactions (the formation of organometallic compounds), and the results of the analogous reactions with aryldiazonium fluoborates. In a number of cases, the diarylbromonium fluoborates led to better results than the diarylbromonium halides. We shall report on this in another communication. In the case of the decomposition of diphenylbromonium slats with metallic bismuth, triphenylbismuth was obtained only from the fluoborate.

We extended this experiment to the decomposition of aryldiazonium salts. The analogy was confirmed. The decomposition of aryldiazonium fluoborates in acetone with metallic bismuth powder (prepared by the precipitation of the metal by the action of zinc dust on an acetone solution of bismuth trichloride) led to the formation (after the action of ammonia — disproportionation) of good yields of triarylbismuth (30-50-70%) for various aromatic radicals. This method was used to prepare triphenylbismuth, tri-p-tolylbismuth, tri-o-tolylbismuth, tri-m-tolylbismuth dichloride, tri-p-bromophenylbismuth, tri-p-chlorophenylbismuth, tri-p-chlorophenylbismuth dichloride, tri-p-carbethoxyphenylbismuth, tri-p-ethoxyphenylbismuth, tri-m-nitrophenylbismuth dichloride, and tri-p-nitrophenylbismuth dichloride.

At the present time, this method of synthesis of organobismuth compounds through the diazocompounds must be considered the best. A possible explanation of the mechanism of the reaction is given in reference [13].

EXPERIMENTAL

The reaction was carried out in a three-necked flask fitted with a Witt stirrer, a reflux condenser, and a thermometer extending to the bottom of the flask.

Metallic bismuth. The bismuth powder was prepared by the action of 20 g of zinc dust on 60 g of bismuth trichloride in acetone. After the product had been sucessively washed with water, hydrochloric acid (15%) alcohol, and ether and dried in air, 37 g of freshly reduced metallic bismuth was obtained.

Triphenylbismuth ($(C_6H_5)_3Bi$). To 9.6 g (0.05 mole) of phenyldiazonium fluoborate in 100 ml of dry acetone was added, with vigorous stirring, 10.5 g (0.05 g-atom) of freshly prepared metallic bismuth. Decomposition of the diazonium salt began immediately, and after 15 minutes it became vigorous. The temperature of the reaction mixture rose to 30-35°. In order to avoid further temperature increase, the reaction mixture was cooled to 25°. N_2 evolution ceased after 15 min. After stirring for 10 min., the mixture was treated successively with 85 ml

of a concentrated solution of ammonia and 330 ml of water. After an hour's standing, the precipitate was suction filtered, washed with water, dried in air, and extracted with benzene in a Soxhlet apparatus. A precipitate crystallized out upon distillation of the benzene. The weight of the raw product was 5.05 g (69% of theoretical). Tar formation was negligible; after recrystallization of the product from alcohol, the m.p. was 77-78°.

The literature value of the melting point is 78° [14].

Tri-p-tolylbismuth ($(p\text{-}CH_3C_6H_4)_3Bi$). Under the conditions of the preceding experiment, 4.66 g (58% of theoretical) of raw tri-p-tolylbismuth was obtained from 10.3 g (0.05 mole) of p-tolyldiazonium fluoborate and 21 g (0.1 g-atom) of bismuth in 100 ml of dry acetone. Recrystallization from alcohol gave 4 g (50% of theoretical) of a material with an m.p. of 115-117°. After a second recrystallization from alcohol, the m.p. was 118-119°.

Literature data: m.p. 116-117° [6]; 119-120° [8].

Tri-o-tolylbismuth ($(o\text{-}CH_3C_6H_4)_3Bi$). Under the conditions of the preceding experiment except that the extraction was carried out with chloroform, tri- o-tolylbismuth was obtained from 10.3 g (0.05 mole) of o-tolyldiazonium fluoborate and 21 g (0.1 g atom) of metallic bismuth in 100 ml of dry acetone. Recrystallization from n-octane gave 4.28 g (54% of theoretical) of a substance with an m.p. of 125-130°. After recrystallization of the material from absolute methyl alcohol, the m.p. was 130-131°.

Literature data: m. p. 130-131° [8].

Found %: C 52.24; 52.38; H 4.48; 4.47. $C_{21}H_{21}Bi$. Calculated %: C 52.28; H 4.41.

Tri-p-ethoxyphenylbismuth ($(p\text{-}C_2H_5OC_6H_4)_3Bi$). 11.8 g (0.05 mole) of p-ethoxyphenyldiazonium fluoborate in 100 ml of dry acetone was decomposed, under the conditions of the preceding experiment, with 24 g (0.11 g-atom) of metallic bismuth. Recrystallization from a mixture of alcohol and ether gave 2.54 g (27% of theoretical) of tri-p-ethoxyphenylbismuth, m.p. 86-87°. With a subsequent recrystallization from absolute methyl alcohol, the substance had an m.p. of 87-88°.

Literature data: m.p. 73° [15].

Found %: C 50.40; 50.51; H 4.80; 4.85. $C_{24}H_{27}BiO_3$. Calculated %: C 50.35; H 4.75.

Tri-p-bromophenylbismuth ($(p\text{-}BrC_6H_4)_3Bi$). Under the conditions of the preceding experiment except that the reaction mixture was preliminarily heated, 13.5 g (0.05 mole) of p-bromophenyldiazonium fluoborate and 16 g (0.08 g-atom) of metallic bismuth in 100 ml of dry acetone gave (after recrystallization from a mixture of n-octane and chloroform) 4.42 g (40% of theoretical) of tri-p-bromophenylbismuth, m.p. 125-130°. After recrystallization of the material from a mixture of acetone and ethyl acetate, 3.45 g (31% of theoretical) of a substance with an m.p. of 140-142° was obtained. Subsequent recrystallization from ethyl acetate gave tri-p-bromophenylbismuth with a m.p. of 147-148°.

Literature data: m.p. 148-149° [9].

Tri-p-chlorophenylbismuth ($(p\text{-}ClC_6H_4)_3Bi$). Under the conditions of the synthesis of tri-p-bromophenylbismuth, 11.3 g (0.05 mole) of p-chlorophenyldiazonium fluoborate and 14 g (0.07 g-atom) of metallic bismuth in 100 ml of dry acetone gave (after two-fold recrystallization from a mixture of chloroform and ethanol (1:1)) 2.84 g (31% of theoretical) of tri-p-chlorophenylbismuth with an m.p. of 100-102°. After recrystallization from a mixture of n-octane and chloroform, the m.p. was 115-116°.

Literature data: m.p. 116° [16].

The tarry residue remaining after the separation of the major product was dissolved in chloroform, the solution was cooled with crushed ice, and chlorine was passed through it for 15 minutes. The residue remaining after evaporation of the chloroform was recrystallized from a mixture of n-octane and chloroform. There was obtained 1.74 g (17% of theoretical) of tri-p-chlorophenylbismuth dichloride with an m.p. of 148-150°. After a second recrystallization from the same solvent, the m.p. was 170°.

Literature data: m.p. 141° [16], 170° [17].

Tri-m-tolylbismuth dichloride ($(m\text{-}CH_3C_6H_4)_3BiCl_2$). 20.6 g (0.1 mole) of m-tolyldiazonium fluoborate was decomposed with 21 g (0.1 g-atom) of metallic bismuth under the conditions of the synthesis of tri-o-tolylbismuth. The reaction product was extracted with chloroform, the chloroform solution was cooled, and chlorine

was passed through it. The residue remaining after evaporation of the chloroform was recrystallized from n-octane; 6.8 g (37% of theoretical) of a substance with an m.p. of 144-147° was obtained. After two-fold recrystallization from n-octane and then from alcohol, the tri-m-tolylbismuth dichloride melted at 151-153°.

Literature data: m.p. 132-133° [18];

Found %: C 45.35; 45.44; H 3.65; 3.83. $C_{21}H_{21}BiCl_2$. Calculated %: C 45.58; H 3.83.

Tri-p-carbethoxyphenylbismuth dichloride ($(p\text{-}C_2H_5OCOC_6H_4)_3BiCl_2$). 13.5 g (0.05 mole) of p-carbethoxyphenyldiazonium fluoborate in 100 ml of dry acetone was decomposed under the above-described conditions with 12 g (0.06 g-atom) of metallic bismuth. The chloroform solution, after chlorine had been passed through it, was evaporated to minimum volume, and 3.9 g (29% of theoretical) of raw tri-p-carbethoxyphenylbismuth dichloride was precipitated from it by the addition of three or four volumes of alcohol. 2.75 g (20% of thoretical) of a substance with an m.p. of 134-137° was obtained by recrystallization from a mixture of n-octane and ethyl acetate. A subsequent recrystallization from the same solvent gave tri-p-carbethoxyphenylbismuth dichloride with an m.p. of 138-139°.

Found %: C 44.83; 44.91; H 3.68; 3.78. $C_{27}H_{27}BiCl_2O_6$. Calculated %: C 44.60; H 3.74.

Tri-p-nitrophenylbismuth dichloride ($(p\text{-}NO_2C_6H_4)_3BiCl_2$). From 12 g (0.05 mole) of p-nitrophenyldiazonium fluoborate and 23 g (0.11 g-atom) of metallic bismuth was obtained, under the conditions of the synthesis of p-carbethoxyphenylbismuth dichloride, 0.8 g (5.5% of theoretical) of raw tri-p-nitrophenylbismuth dichloride. After recrystallization from a mixture of acetone and alcohol, the m.p. was 160-161° (with decomposition).

Found %: N 6.31; 6.37. $C_{18}H_{12}BiCl_2N_3O_6$. Calculated %: N 6.5.

Tri-m-nitrophenylbismuth dichloride ($(m\text{-}NO_2C_6H_4)_3BiCl_2$). To 18 g (0.075 mole) of m-nitrophenyldiazonium fluoborate in 150 ml of dry acetone was added 34 g (0.16 g-atom) of metallic bismuth. The reaction proceeded sluggishly in the cold; therefore, the reaction mixture was heated over 2 hours to 50-56°. Further treatment was as in the preceding experiment. 3.7 g (26% of thoretical) of raw tri-m-nitrophenylbismuth dichloride was obtained. After two-fold recrystallization from ethyl acetate and chloroform, the m.p. was 131-132°.

Literature data : m.p. 132-134° [18]*

Found %: C 33.50; 33.43; H 2.08; 2.04; N 6.48. $C_{18}H_{12}BiCl_2N_3O_6$. Calculated %: C 33.47; H 1.87; N 6.50.

LITERATURE CITED

[1] A. N. Nesmeianov, J. Russ. Phys. Chem. Soc., 61, 1393 (1929); Ber., 62, 1010 (1929); A. N. Nesmeianov and E. I. Kan, J. Russ. Phys. Chem. Soc. 61, 1407 (1929); Ber., 62, 1018 (1929); A. N. Nesmeianov and L. G. Makarova, J. Gen. Chem., 1, 538 (1931); A. N. Nesmeianov, N. F. Glushnev, P. F. Epifanskii and A. I. Flegontov, J. Gen. Chem., 4, 713 (1934); Ber., 67, 130 (1934); A.N. Nesmeianov, Sci. Records Moscow State Univ., 3, 291 (1934); A. N. Nesmeianov and E. M. Toropova, J. Gen. Chem., 4, 664 (1934).

[2] A. N. Nesmeianov and L. G. Makarova, Proc. Acad. Sci. USSR, 87, 417 (1952).

[3] A. N. Nesmeianov, K. A. Kocheshkov and V. A. Klimova, J. Gen. Chem., 6, 167 (1936); Ber., 68, 1877 (1935).

[4] K. A. Kocheshkov, A. N. Nesmeianov and N. K. Gipp, J. Gen. Chem., 6, 172 (1936).

[5] A. N. Nesmeianov and K. A. Kocheshkov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1944, 416; A. N. Nesmeianov, N. K. Gipp and L. G. Makarova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, 298;** O.A. Reutov and O. A. Ptitsyna, Proc. Acad. Sci. USSR, 79, 819 (1951).

[6] H. Gilman, A. Svigoon, J. Am. Chem. Soc., 61, 3586 (1939); H. Gilman, H. L. Jablunsky, J. Am. Chem. Soc., 63, 949 (1941).

* Tri-m-nitrophenylbismuth dichloride was first obtained by Supniewski and Adams [18], but the authors incorrectly considered it to be tri-p-nitrophenylbismuth dichloride. Vorlander [19] was able to show later that the original dinitrate was the meta compound. Our method confirms the point of view of Vorlander.

** Original Russian pagination. See C. B. Translation.

[7] K. A. Kocheshkov, M. M. Nad'and T. K. Kozminskaia, Bull. D. I. Mendeleev All-Union Chem. Soc., 9, 20 (1940).

[8] T. K. Kozminskaia, M. M. Nad'and K. A. Kocheshkov, J. Gen. Chem., 16, 891 (1946).

[9] M. M. Nad', T. K. Kozminskaia and K. A. Kocheshkov, J. Gen. Chem., 16, 897 (1946).

[10] A. N. Nesmeianov, K. A. Kocheshkov and M. M. Nad', Bull. Acad. Sci. USSR, Div. Chem. Sci., 1945, 522.

[11] A. N. Nesmeianov and L. G. Makarova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, 380. *

[12] A. N. Nesmeianov and L. G. Makarova, Proc. Acad. Sci. USSR, 87, 421 (1952).

[13] A. N. Nesmeianov, L. G. Makarova, T. P. Tolstaia, Tetrahedron, 1, 145 (1957).

[14] P. Pfeiffer, H. Pietsch, Ber., 37, 4622 (1904).

[15] A. Gillmeister, Ber., 30, 2850 (1897).

[16] F. Challenger, L. R. Ridgway, J. Chem. Soc., 121, 109 (1922).

[17] H. Gilman, H. Jale, Chem. Rev., 30, 307 (1942).

[18] J. V. Supniewski, R. Adams, J. Am. Chem. Soc., 48, 507 (1926).

[19] D. Vorlander, Ber, 58, 1893 (1925).

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PREPARATION AND PROPERTIES OF SOME TRICHLOROTITANIUMALKOXY COMPOUNDS (ALKOXYTITANIUM TRICHLORIDES) WITH SECONDARY AND TERTIARY ALKYL GROUPS

Corresponding Member AN SSSR G. A. Razuvaev, L. M. Bobinova and V. S. Etlis

For some time past, there has been a considerable increase in the interest in organotitanium compounds as possible intermediate products of the reaction of trialkylaluminums with titanium tetrachloride, which, in the opinion of some authors [1], are the initiators of the polymerization of olefins. There are indications of the preparation of systems containing organic titanium compounds which are active catalysts for the polymerization of olefins [2, 3].

Natta and co-workers [4] investigated the effect on the activity of Ziegler catalyst of the replacement of the chlorine in $TiCl_4$ by alkoxy groups, and they obtained an active catalyst for the polymerization of olefins by supporting tetraisopropoxytitanium on an aluminosilicate carrier in the presence of triethylaluminum.

In the present work, we prepared and studied the properties, including catalytic activity for the polymerization of olefins, of some titanium compounds of the type $TiCl_3OR$ where R is a secondary or tertiary group; these compounds, in contrast to the well-studied similar compounds where R is a primary radical [5], are not well known in the literature. In the synthesis of isopropoxytitanium trichloride from $TiCl_4$ and $Ti(i\text{-}OC_3H_7)_4$ by a radical exchange reaction which has been described in the literature [6, 7], the compound obtained was not sufficiently pure. Pure $i\text{-}C_3H_7OTiCl_3$, free from impurities, was synthesized from isopropyl alcohol and excess $TiCl_4$ in solution in petroleum ether (b.p. 60-70°) at a temperature of about 0°. During the synthesis, some insoluble material precipitated from solution; this material was filtered. The filtrate was distilled to remove part of the solvent, after which cooling precipitated crystals of pure isopropoxytitanium trichloride, $sec\text{-}C_4H_9OTiCl_3$ and $C_6H_{11}OTiCl_3$,* neither of which have previously been described in the literature, were prepared by an analogous method except that distillation of the petroleum ether was carried out under vacuum at a temperature of 25-30° to decrease the decomposition of these compounds (Table 1).

TABLE 1

Compound	Yield, %	Outward appearance	M.p. °C	Found, %			Calculated, %		
				Ti	Cl	RO	Ti	Cl	RO
$i\text{-}C_3H_7OTiCl_3$	70—75	Tablets (from petroleum ether), light yellow color	78—79	22,50	49,80	27,50	22,45	49,90	27,65
$sec\text{-}C_4H_9OTiCl_3$	52—56	Same	54—56	21,03	46,50	32,0	21,05	46,85	32,10
$C_6H_{11}OTiCl_3$	41—43	"	75—76	18,4	41,8	—	18,9	42,0	—

It was established that, in contrast to similar compounds with primary groups, the compounds synthesized are unstable. A precipitate, the analysis of which corresponded to titanium oxychloride, separated from solutions

*C_6H_{11}– is cyclohexyl.

of these compounds in benzene or petroleum ether on standing. On storage in a sealed tube, the solid products decomposed rapidly with the evolution of gaseous compounds and the formation of titanium oxychloride. In order to study the decomposition process, the freshly prepared pure compounds were decomposed at a temperature of 45-50° over the course of 15-20 hours to the complete decomposition of the compounds; the resulting gaseous and liquid compounds were collected. In the case of sec-$C_4H_9OTiCl_3$ and $C_6H_{11}OTiCl_3$, isolation of the liquid products was carried out under vacuum (100-150 mm residual pressure). The following products of the decomposition of the $TiCl_3OR$ compounds (where R is i-C_3H_7, sec-C_4H_9, or C_6H_{11}) were identified: HCl; the alkyl chlorides i-C_3H_7Cl, sec-C_4H_9Cl, and $C_6H_{11}Cl$, respectively; titanium oxychloride; and olefin polymerization products, which were strongly adsorbed on the surface of the oxychloride, and could be only partially removed by washing with a solvent. A material balance for the decomposition of the above-indicated organotitanium compounds is presented in Table 2.

TABLE 2

Material Balance for the Decomposition of $TiCl_3OR$ Compounds (where R is i-C_3H_7, sec-C_4H_9, and C_6H_{11})

Substance	Wt.	Decomposition products								Σ	
		Titanium oxychloride		HCl		RCl		Polymerization products			
		g	%	g	%	g	%	g	%	g	%
i-$C_3H_7OTiCl_3$	29,54	19,78	67,00	1,85	6,27	6,14	20,80	1,40	4,75	29,17	98,82
	22,13	14,98	67,69	0,96	4,33	5,36	24,24	0,81	3,66	22,11	99,92
	24,55	16,25	66,30	1,75	7,14	4,98	20,35	1,15	4,68	24,13	98,47
sec-$C_4H_9OTiCl_3$	14,10	9,68	68,65	0,84	5,96	1,87	13,35	1,47	10,44	13,86	98,40
	15,20	8,76	57,65	1,13	7,44	3,83	25,20	1,39	9,15	15,11	99,44
$C_6H_{11}OTiCl_3$	11,82	4,88	41,32	0,84	7,10	4,17	35,27	0,22	1,87	10,11	85,56
	23,60	10,00	42,45	0,64	2,71	11,24	47,66	0,13	0,56	22,01	93,38
	24,13	12,45	51,65	1,70	7,05	9,40	38,80	0,20	0,83	23,75	98,33

An attempt to synthesize tert-$C_4H_9OTiCl_3$ by a similar method was unsuccessful owing to the decomposition of the product, as it was formed, to titanium oxychloride. Tertiary butyl chloride and isobutylene polymer were isolated from the solution.

In Table 3 are presented the physicochemical properties of the products obtained by the decomposition of the titanium compounds described above. In the case of the $C_6H_{11}TiCl_3$, the incomplete material balance (Table 2) and the insufficient chlorine content of the titanium oxychloride (Table 3) are explained by the fact that during the separation of the liquid products under vacuum, a certain amount of titanium tetrachloride accompanied the HCl; this was condensed along with the cyclohexyl chloride, and was determined in the water from the washing of the $C_6H_{11}Cl$.

On the basis of the decomposition products isolated, it can be assumed that the primary process in the decomposition of $TiCl_3OR$ compounds (where R is a secondary or tertiary radical) is the formation of titanium oxychloride and radicals which can give olefin and HCl or alkyl chloride.

The formation of alkyl chlorides in the succeeding reactions by hydrochlorination of the olefins is possible; the presence in the decomposition products of olefins and HCl can indicate the occurrence of the reverse reaction – the dehydrochlorination of alkyl chlorides. The polymer was obviously formed by polymerization of olefins.

In order to establish the possible directions of the decomposition reactions, we studied the catalytic activity, with respect to olefin hydrochlorination and alkyl chloride dehydrochlorination, of titanium oxychloride prepared by the decomposition of the above-indicated compounds. It was shown that this compound is an effective catalyst for the hydrochlorination of propylene, isobutylene, and cyclohexene, which react to form the analogous alkyl chlorides in good yield. The reverse reaction – dehydrochlorination of the alkyl chlorides – did not proceed under the conditions of the decomposition of the original organotitanium compounds.

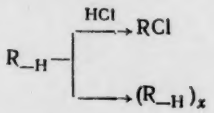
TABLE 3

Physicochemical Characteristics of the Products from the Decomposition of $TiCl_3OR$ Compounds, where R is a Secondary or Tertiary Group

Initial material	Alkyl chloride						Ti oxychloride, comp., %			Polymerization product					
	B.p. °C		n_D		Cl, %		Ti	Cl	RO group	n_D^{20}	M	Bromine number	Found, %		Calc. for $(C_nH_{2n})_m$ %
	Found	Lit.	Found	Lit.	Found	Calc.							C	H	C H
i-$C_3H_7OTiCl_3$	34,5—35	34,8	n_D^{18} 1,3810	1,3811	44,9	45,2	30—31	46,5—47	3—5	1,4562	208	114	85,61	13,80	85,7 14,3
sec-$C_4H_9OTiCl_3$	65,7—68	68	n_D^{20} 1,3951	1,3953	38,6	38,4	27—29	42—45	5—6	1,4690	269	196	85,8	13,73	85,7 14,3
$C_6H_{11}OTiCl_3$	140—141	142	n_D^{18} 1,4558	1,4555	29,5	29,9	30—32	34—37	—	1,4800	249	186	85,5	12,04	86,8 12,2
tert-$C_4H_9OTiCl_3$	50—52	51—2	n_D^{18} 1,3872	1,3869	37,8	38,4	25—27	47—49	—	1,4800	224	260	85,4	13,2	85,7 14,3

On the basis of our results, we propose the following scheme for the decomposition of $TiCl_3OR$, where R is a secondary or tertiary group:

$$TiCl_3 - OR \rightarrow TiOCl_2 + R_{-H} + HCl$$



The titanium oxychloride obtained by this method is an effective catalyst for the polymerization of propylene to give a mixture of unsaturated hydrocarbons in the molecular weight range of 86-428° (polymerization temperature, 90-100°; time, 3-4 hours; polymer yield, 95-98%)* and also for the polymerization of isobutylene and styrene, the reaction proceeding at low temperatures with the formation of liquid and semi-solid products. This compound is also a catalyst for certain Friedel-Crafts reactions, particularly for the alkylation of benzene with olefins with the formation of the corresponding alkylbenzenes. The alkylation of benzene with ethylene, propylene, and cyclohexene was carried out in the presence of this catalyst, and ethylbenzene, isopropylbenzene, and cyclohexylbenzene, respectively, were formed together with small amounts of di- and trisubstituted alkylbenzenes.

LITERATURE CITED

[1] C. D. Nenitzescu, Rev. Chim., 10, 573 (1956).

[2] G. Natta, P. Pino et al., J. Am. Chem. Soc., 79, 2957 (1957).

[3] D. Young, H. Kellog, U.S. Pat. 2440498, April 27, 1948.

[4] G. Natta, P. Pino, P. Londi, Gazz. Chim. Ital., 87, 570 (1957).

[5] A. N. Nesmeianov, R. Kh. Friedlina and O. V. Nogina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1952, 1037.**

[6] D. Bradley, D. Hancock, W. Wardlaw, J. Chem. Soc., 1952, 2273.

[7] A. N. Nesmeianov, E. M. Brainina and R. Kh. Friedlina, Proc. Acad. Sci. USSR, 94, No. 2, 249 (1954).

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* Titanium oxychloride prepared by partial hydrolysis of titanium tetrachloride with water was shown to be only slightly active for the polymerization of olefins.

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INVESTIGATION OF THE PARAFFINIC HYDROCARBONS OF THE KEROSENE FRACTION OF AKTASH CRUDE FROM THE ROMASHKIN FORMATION

L. M. Rozenberg, Academician A. V. Topchiev, I. B. Ushakova, I. S. Genekh, N. I. Liashkevich, E. M. Terent'eva and P. A. Nikitina

The study of the composition and properties of the paraffinic hydrocarbons of high-boiling fractions of petroleum is attended by considerable experimental difficulties.

The composition of the paraffinic hydrocarbons of the low-boiling fractions of petroleum (up to 150°) has been studied the best. Among the investigations of the paraffinic hydrocarbons of kerosene fractions, we may mention the work of Rossini et al [1], who separated from Ponca City crude the normal C_{10} to C_{17} paraffins, inclusive, in 97-99% purity.

Kh. M. Areshidze and E. M. Benashvili [2] obtained C_{12}-C_{15} hydrocarbons in purities above 95% from the 200-250° fraction of Noric crude.

A. V. Topchiev, S. S. Nifontova et al.[3] studied the content of n-paraffins in 25-degree fractions of Romashkin kerosene by isolating the n-paraffins with urea. The resulting narrow fractions of individual hydrocarbons were close in physicochemical properties to C_{10} to C_{18} straight-chain paraffins. V. G. Nikolaeva, E. V. Zvereva et al.[10] isolated the C_{12}-C_{20} n-paraffins in purities of 90-100% from the 200-350° fraction of Romashkin petroleum. Each of the isolated hydrocarbons comprised about 2% of the 200-350° fraction, and the total amount of n-paraffins was 16%.

The present investigation was undertaken with the aim of obtaining qualitative and quantitative characterization of the n-paraffinic hydrocarbons of the kerosene fraction (175-300°) of Aktash crude from the Romashkin formation.

Aktash crude from the Romashkin formation is a Devonian crude from the Mikhailov horizon D_0; our sample, which was taken from crude produced May 24, 1956, from well No. 94 at a depth of 1583-1585.8 meters, was topped through the gasoline fraction in a single-stage vaporization apparatus. Next, in order to obtain distillates changed from the crude as little as possible, the topped (to 175°) crude was deasphalted by the cold distillation method developed at the Institute of Petroleum AN SSSR. The topped and deasphalted crude was distilled in a VNII NP [All-Union Scientific Research Institute for the Processing of Petroleum and Gas and for the Production of Synthetic Liquid Fuel] vacuum apparatus. The kerosene fraction, 175-300°, was collected; the yield was 17.2% of the crude.

After removal of the aromatic and sulfur compounds by adsorption on silica gel, the product, in an amount of 10.4 kg, was treated with urea [4]. 2.5 kg of hydrocarbons reacting with urea were obtained; this amounts to 24.3 wt. % of the dearomatized fraction, 18.4 wt. % of the original (175-300°) fraction, and 3.16% wt. % of the crude. Properties of this material: $d^{20}_{4} = 0.7639$; f.p. −2°. This product was treated, over a period of 3 hours on a boiling water bath, with, successively, two volumes and then one volume of 100% sulfuric acid to remove the isomers.

After treatment of the product with acid and the removal of 10% isomers, the freezing point increased from −2 to −0.5°.

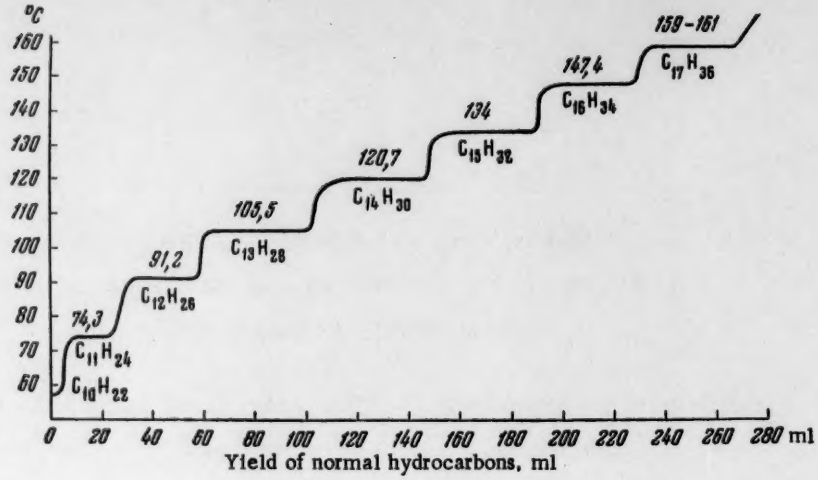

Fig. 1

The paraffins were then subjected to precise fractionation in a vacuum column. The amount of isomers of the n-paraffins was checked by a method proposed by us [5] involving a qualitative color reaction of hydrocarbons having a tertiary carbon atom in the molecule with $FeCl_3$ and $K_3Fe(CN)_6$. Each of the major fractions collected contained the respective individual n-paraffinic hydrocarbons without the isomeric hydrocarbons. The latter were concentrated in the fractions cut between the plateaus, which gave a positive reaction with $FeCl_3$. The freezing point of the combined intermediate cuts was −9°.

TABLE 1

Distillation of the Paraffinic Hydrocarbons from Aktash Crude. 231.15 g charged to the distillation.

Fraction	n-Paraffin yield				B.p.°C at 10 mm Hg		Qual. reaction with $FeCl_3$ *
	in g	in wt. %					
		of paraffin fract.	of kerosene	of crude	Exptl. data	Lit. data [8]	
$C_{10}H_{22}$	3,47	1,50	0,25	0,04	57,3—57,5		—
Intermediate	4,64	2,0	0,33	—	57,5—74,3		+
$C_{11}H_{24}$	12,39	5,35	0,88	0,15	74,3	75	—
Intermediate	4,73	2,04	0,34	—	76—90,3		+
$C_{12}H_{26}$	20,41	8,83	1,46	0,25	91,2	91,5	—
Intermediate	3,0	1,29	0,21		92—105,5		+
$C_{13}H_{28}$	30,23	13,07	2,16	0,37	105,5	106,8	—
Intermediate	7,55	3,26	0,54		105,5—120,5		+
$C_{14}H_{30}$	28,46	12.31	2,04	0,35	120,5—120,7	120,5	—
Intermediate	6,81	2,94	0,48		120,7—134		+
$C_{15}H_{32}$	26,89	11,63	1,92	0,33	134	135,4	—
Intermediate	6,6	2,85	0,47	—	134,1—147,7		+
$C_{16}H_{34}$	22,83	9,87	1,63	0,28	147,4—147,5	148,7	—
Intermediate	6,06	2,63	0,43	—	148—160	—	+
$C_{17}H_{36}$	21,8	9,46	1,56	0,27	160—161	161,5	—
Residue, 161,0	17,54	7,61	—	—			+
Loss	7,74	3,36	—	—			

* Minus — negative raction; plus — positive reaction.

The results of the distillation and the yields of paraffinic hydrocarbons are presented in Table 1 and Figure 1; the properties and purities of the individual hydrocarbons isolated from the kerosne of Aktash crude are presented in Table 2.

TABLE 2

Composition and Properties of the n-Paraffins Isolated from the 170-300° Fraction of Aktash Crude (Well No. 94)

Hydrocarbon	d_4^{20}	n_D^{20}	Mol. wt.	Crystallization Temp., °C		Degree of purity, mol. %
				Exptl. Data*	Lit. Data [9]	
Decane . . .	0,7296	1,4128	142	−30,5	−29,67	98,48
Undecane. .	0,7398	1,4178	156	−25,8	−25,65	99,70
Dodecane. .	0,7488	1,4226	170	−9,85	−9,60	98,59
Tridecane. .	0,7560	1,4268	184	−5,6	−6,0	98,58
Tetradecane	0,7630	1,4299	198	+5,2	+5,5	98,81
Pentadecane	0,7684	1,4329	212	+9,7	+9,8	97,833
Hexadecane	0,7743	1,4358	226	+17,5	+18,15	97,27
Heptadecane	0,9922**	1,4368	240	+21,3	+21,72	95,62
Residue	0,7720**	—	—	+27,5		

* Crystallization temperature determined from the melting point curve.

** At 40°.

The hydrocarbon purities were quantitatively evaluated by thermodynamic analysis of the melting point – time curves, which were obtained using the apparatus and method developed at the Institute of Petroleum AN SSSR [6,7].

In accordance with this method, a weighed sample, 0.04-0.05 g, was heated in a Duralumin block, the temperature of which was raised at a constant rate of 0.3°/minute. This heating rate was maintained by means of a phototube–thyratron relay adapted for program control at a the proper temperatures in an interval of the order of 20°.

During heating of the block, the e.m.f. of a platinum-gold-palladium thermocouple located in the sample was measured with a PPTN-1 potentiometer.

From the resulting graphs showing the change in e.m.f. with time, the melting point of the sample and the depression due to the impurity were determined; the degree of purity of the investigated hydrocarbons was evaluated from these figures.

It was found that of the hydrocarbons isolated by means of urea, not less than 75-80% were normal paraffins. By treatment of the product with 100% sulfuric acid and precise fractionation under vacuum, it was possible to obtain complete removal of the isomers, which concentrated in the intermediate cuts. The plateau fractions were pure, individual straight-chain paraffins.

Thus, by applying this method to Aktash crude from Romashkin formation the feasibility of separating from the 175-300° fraction the normal paraffinic hydrocarbons, uncontaminated by isomers, with a purity of 97.2-99.7% was demonstrated.

The distribution of the n-paraffins in the 175-300° kerosene of Aktash crude is as follows (in wt. %): $C_{10}H_{22}$, 0.25; $C_{11}H_{24}$, 0.88; $C_{12}H_{26}$, 1.46; $C_{13}H_{28}$, 2.16; $C_{14}H_{30}$, 2.04; $C_{15}H_{32}$, 1.92; $C_{16}H_{34}$, 1.63; $C_{17}H_{36}$, 1.56.

C_{13}-C_{15} hydrocarbons comprised 50% of the total of all n-paraffins in the 175-300° fraction.

LITERATURE CITED

[1] F. D Rossini, B. J. Mair and A. J. Streiff, Hydrocarbons from Petroleum.[Translated from English]. Leningrad, 1957.

[2] Kh. I. Areshidze and E. M. Benashvili, Proc. Acad. Sci. USSR, 110, No. 3, 387 (1957).*

*Original Russian pagination. See C. B. Translation.

[3] A. V. Topchiev, S. S. Nifontova, R. Ia. Sushchik and A. A. Suchkova, Proc. Acad. Sci. USSR, 111, No. 5, 1045 (1956).*

[4] L. M. Rozenberg, I. S. Genekh and P. A. Nikitina, Azerb. Petroleum Ind., No. 12, 18 (1953).

[5] E. M. Terent'eva and L. M. Rozenberg, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1957, 1144.**

[6] A. V. Topchiev and N. I. Liashkevich, Annotations on the Papers on the Chemistry and Technology of Petroleum and Gas for 1956, Moscow, Institute of Petroleum AN SSSR, 1957, p. 8.**

[7] N. I. Liashkevich, An Electronic Heating Rate Controller for Thermal Analysis in Narrow Temperature Ranges, Moscow, 1957. **

[8] M. D. Tilicheev and A. V. Iogansen, J. Phys. Chem., 24, No. 7, 770 (1950).

[9] Physicochemical Properties of Individual Hydrocarbons, ed. by M. D. Tilicheev, Moscow-Leningrad, 1953.**

[10] V. G. Nikolaeva and E. V. Zvereva, Chem. and Technology of Fuels, No. 3, 11 (1956).

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** In Russian.

ON THE REACTION MECHANISM OF THE CATALYTIC HYDROGENOLYSIS OF THE FURAN RING

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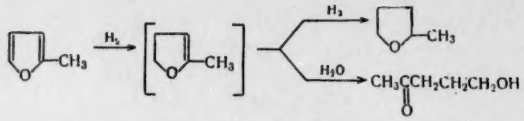
During investigations of the hydrogenolysis of furan and its derivatives, various authors have posed the question of the possibility of this reaction proceeding through a stage in which the double bonds in the ring are hydrogenated with subsequent cleavage of the resulting tetrahydrofuran ring at one of the C—O bonds. A negative answer was given to this question by investigations comparing the hydrogenolysis of furan and its derivatives, on the one hand, and of the corresponding tetrahydro derivatives, on the other, under uniform reaction conditions. Thus, Kaufmann and Adams [1], as a result of an investigation of the behavior of furfuryl and tetrahydrofurfuryl alcohols under liquid-phase hydrogenation conditions over platinum catalyst, came to the conclusion that the formation of 1,2-pentanediol and 1,5-pentanediol during hydrogenation of furfuryl alcohol cannot proceed through a stage in which the double bonds in the ring are reduced, since tetrahydrofurfuryl alcohol does not undergo hydrogenolysis to an appreciable extent.

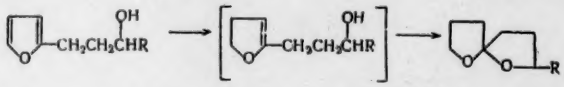
Smith and Fuzek [2] arrived at similar ideas regarding the mechanism of the hydrogenolysis of the furan ring during a study comparing the hydrogenolysis of furan and tetrahydrofuran in solution in acetic acid in the presence of the same catalyst. Connor and Adkins [3] investigated the liquid-phase hydrogenolysis of sylvan and tetrahydrosylvan and of furfuryl and tetrahydrofurfuryl alcohols over copper chromite, and they found a sharply different behavior of furan and tetrahydrofuran rings toward hydrogenolysis. Tetrahydrofurfuryl alcohol, which underwent hydrogenolysis to only a slight extent, gave exclusively 1,5-pentanediol, while under the same conditions, furfuryl alcohol was converted into a mixture of almost equal amounts of 1,2-pentanediol and 1,5-pentanediol. Under identical hydrogenation conditions, sylvan gave a 70% yield of hydrogenolysis products, while 74% of the tetrahydrosylvan was unchanged.

Thus, the investigations enumerated above showed that the tetrahydrofuran ring lacks completely that ability to undergo hydrogenolysis under liquid phase hydrogenation conditions which is, to a high degree, a property of the furan ring. This difference in the behavior of the furan and tetrahydrofuran rings under catalytic hydrogenation conditions is also present when the reactions are carried out in the vapor phase over nickel [4] or skeletal nickel-aluminum [5] catalysts. Wilson [4] compared the hydrogenolysis of sylvan with that of tetrahydrosylvan in the vapor phase over a nickel catalyst, and he found that tetrahydrosylvan remains unchanged at 100°, but undergoes extensive decomposition of the ring at 250° with the formation of gaseous products. Consequently, that hydrogenation of the double bonds in the furan ring does not precede hydrogenolysis of the ring also holds under vapor-phase conditions.

We have recently shown that homologs of tetrahydrofuran are isomerized to aliphatic ketones over Pt/carbon at 250-300°. However, this reaction proceeds much more slowly than the direct hydrogenolysis of these same alkylfurans under the same conditions, and, therefore, it is impossible to assume that tetrahydrofurans are intermediate compounds in the hydrogenolysis of furan compounds. Thus, all of these investigations lead to the conclusion that hydrogenolysis of the C—O bond must take place either in the ring of the furan itself or in the ring of dihydrofuran. The formation of the latter as an intermediate product is shown by the conversion of sylvan to γ-acetopropyl alcohol [5-hydroxy-2-pentanone] during hydrogenation in the presence of water [7]:

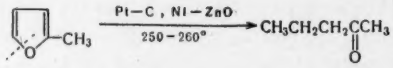


The formation of spiranes from 3-furfurylalkanols under hydrogenation conditions over nickel and copper-chromium catalyst is also indirect proof of the stepwise hydrogenation of bonds in the furan ring. Alexander and co-workers [8] proposed the following scheme for the formation of spiranes:

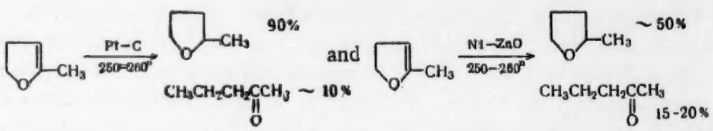


On the basis of these experimental data, some investigators [4, 9] assume the formation of dihydrofuran to be an intermediate stage in the hydrogenolysis of the furan ring. At the same time, Bredley [10], in measuring the rate of hydrogenation of furan over platinum catalyst, found that the addition of 3 moles of hydrogen does not proceed stepwise, since all of the hydrogenation curves were smooth. This fact, together with the material cited above, can be interpreted to mean that hydrogenation in the presence of water creates conditions favorable to a different reaction route, and that the answer to the question of which of the mechanisms proposed for the hydrogenolysis of the furan ring is correct cannot be given by the results of hydrogenation of the furan ring in the presence of water.

In the present work, we investigated the vapor-phase hydrogenation of dihydrosylvan over platinized carbon and over nickel on zinc oxide at 250-260°. As is well known, sylvan, under these conditions, is cleaved only at the 1,5-C–O bond with the formation of methyl propyl ketone [11]. Tetrahydrosylvan is unchanged by Ni/ZnO, and in the presence of Pt/C it undergoes isomerization to 2-pentanone [6]; the rate of formation of ketone in this case is significantly lower than the rate of its formation as a result of hydrogenolysis of sylvan:



Dihydrosylvan, if it is formed as an intermediate compound during the hydrogenolysis of sylvan, would have to be converted to methyl propyl ketone with the same ease and just as completely as sylvan. However, our experiments show that the main reaction during hydrogenation of dihydrosylvan over Pt/C and Ni/ZnO at 250-260° is not hydrogenolysis of a C–O bond, but hydrogenation of the carbon-carbon double bond in the ring:

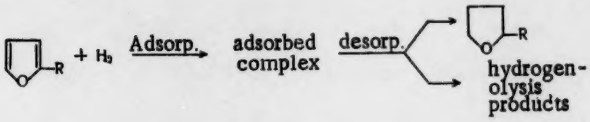


The formation of methyl propyl ketone during the hydrogenation of dihydrosylvan over Pt/C can occur as a result of a secondary isomerization reaction of tetrahydrosylvan. Tetrahydrosylvan does not isomerize to methyl propyl ketone over Ni/ZnO; therefore, in this case it must be assumed that the dihydrosylvan undergoes hydrogenolysis at the 1,5-C–O bond with the formation of 2-pentanone. During hydrogenation of dihydrosylvan over Ni/ZnO, in addition to tetrahydrosylvan and methyl propyl ketone, a considerable amount (30-35%) of a compound with a high boiling point was formed.

The ability of the C=C bond in the dihydrosylvan ring to undergo hydrogenation easily is obviously connected with the fact that this bond possesses the properties of a simple olefinic bond. As a consequence of this, it must undergo hydrogenation with approximately the same ease as the double bond in the side chain of

alkenylfurans and significantly more easily than the C–O bond in the dihydrofuran ring. In addition, according to deductions based on the multiplet theory [12], hydrogenation of the first double bond in the furan ring proceeds considerably more difficultly than hydrogenation of an olefinic bond and approximately with the same ease as hydrogenolysis of the C–O bond in the furan ring. Hence, it follows that rupture of the C–O bond in the furan ring itself is considerably more probable; this finds complete confirmation in our experiment.

It is possible to give our results another interpretation. It is possible to assume that the sylvan ring, in the adsorbed state, is hydrogenated first at one C=C bond, and then this adsorbed dihydrosylvan can undergo further hydrogenation to tetrahydrosylvan, can undergo hydrogenolysis, or, finally, can add the elements of water across the double bond. The experiment shows that if only one C=C bond in the furan ring can be hydrogenated initially, then this product of partial reduction must, without desorbing, undergo further conversions in the directions indicated above. In general, the method of proving a mechanism of hydrogenolysis of the furan ring which consists of investigating the behavior of possible intermediate forms (in our case, dihydrosylvan and tetrahydrosylvan) under uniform reaction conditions cannot answer the question of the succession in which the hydrogenation processes proceed on the surface of the catalyst, since a mechanism in fact includes consideration of the adsorption and desorption stages of the intermediate compounds. Taking into consideration all of the material presented above, it is possible, on the basis of our experiments, to confirm that the formation of dihydrosylvan is not an intermediate stage in the hydrogenolysis of the furan ring. In other words, after a series of elementary acts in the process of hydrogenation of the furan ring, either tetrahydro derivatives or products of the hydrogenolysis of the ring at an ether bond are desorbed from the surface of the catalyst:



EXPERIMENTAL

Catalysts. The platinized carbon was prepared by impregnation of activated carbon with the calculated amount of a solution of chloroplatinic acid and subsequent reduction with hydrogen in the reaction tube at 200-250°. The catalyst contained 5% of finely dispersed platinum. The Ni/ZnO, which contained 30% Ni, was prepared by coprecipitation of nickel and zinc hydroxides from a solution of their nitrates, using potassium hydroxide as the precipitant, and subsequent reduction with hydrogen at 200-300°.

Starting materials. The dihydrosylvan was prepared by dehydration of acetopropyl alcohol [5-hydroxy-2-pentanone] by the method of Kyrides and Zienty [13]. After distillation in an efficient column, it had the following constants: b.p. 79-80°/750 mm; d^{20}_4 0.9039 and $n^{20}D$ 1.4297. Found MR 24.02; calculated for C_5H_8O MR 24.26. Pure sylvan (b.p. 64-66/750 mm, d^{20}_4 0.9121, $n^{20}D$ 1.4320) was separated from the commercial products by treatment of the latter with sodium and distillation in an efficient column. The experiments comparing

TABLE 1

Products of the Hydrogenation of Sylvan and Dihydrosylvan Over Pt/C and Ni/ZnO at 250-260°

Starting material	Products of hydrogenation over Pt/C	Products of hydrogenation over Ni/ZnO
Sylvan	2-Pentanone (~100%): b.p. 109*-101.5°, d^{20}_4 0.8080, $n^{20}D$ 1.3912	2-Pentanone (95-100%)
Dihydro-sylvan	Tetrahydrosylvan (90%); b.p. 79-80° d^{20}_4 0.7582, $n^{20}D$ 1.4060 2-Pentanone (~10%)	Tetrahydrosylvan (50%), 2-pentanone (15-20%), compound with a b.p. above 105° (30-35%)

*As in original. 100° is probably the correct value – Publishers note.

the hydrogenation of sylvan with that of dihydrosylvan were carried out by the flow method at ordinary pressure. The temperature was measured with an alumel–chromel thermocouple in the center of the catalyst bed. The material was fed to the reaction zone at a space rate of 0.1 hours $^{-1}$. The catalyzates were dried with potassium carbonate, and distilled in a column with an efficiency of 40 theoretical plates.

The results are presented in Table 1.

LITERATURE CITED

[1] W. Kaufmann, R. Adams, J. Am. Chem. Soc., 45, 3029 (1923).

[2] H. Smith, J. Fuzek, J. Am. Chem. Soc., 71, 415 (1949).

[3] R. Connor, H. Adkins, J. Am. Chem. Soc., 54, 4687 (1932).

[4] C. Wilson, J. Am. Chem. Soc., 70, 1313 (1948).

[5] N. I. Shuikin, V. A. Tulupov and I. F. Bel'skii, J. Gen. Chem., 25, 1175 (1955).*

[6] N. I. Shuikin and I. F. Bel'skii, Proc. Acad. Sci. USSR, 120, 548 (1958). *

[7] K. S. Topchiev, Proc. Acad. Sci. USSR, 19, 497 (1938); L. Schniepp, H. Geller, R. Korff, J. Am. Chem. Soc., 69, 672 (1947).

[8] K. Alexander, L. Hafner, G. Smith, L. Schniepp, J. Am. Chem. Soc., 72, 5506 (1950); 73, 2725 (1951).

[9] A. P. Dunlop, F. N. Peters, The Furans, Am. Chem. Soc., Monogr. Ser., N. Y., 1953.

[10] C. W. Bredley, Iowa State Coll. J. Sci., 12, 108 (1937); Chem. Abstr. 32, 2531 (1938).

[11] N. I. Shuikin and I. F. Bel'skii, Proc. Acad. Sci. USSR, 116, 621 (1957). *

[12] A. A. Balandin and A. A. Ponomarev, J. Gen. Chem, 26, 1146 (1956).*

[13] L. Kyrides, F. Zienty, J. Am. Chem. Soc., 68, 1385 (1946).

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NEW CARBON-SUBSTITUTED DERIVATIVES OF GLUCOSE

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(Presented by Academician A. I. Oparin June 4 1958)

We have previously synthesized various carbon-substituted derivatives of glucose, containing such radicals as naphthyl, tolyl, diphenyl, thienyl, phenetyl, p-anisyl, etc. [1]. The general method used for obtaining compounds of this type was organomagnesium synthesis.

The present paper describes the synthesis of o-anisyltetracetylglucose and its bromo and nitro derivatives. The nitro derivative of p-anisyltetracetylglucose which we had previously obtained was reduced to the corresponding amine. It should be noted that the best method of reduction was hydrogenation in the presence of Raney nickel; other method (reduction with zinc, iron, tin) did not give clear results.

The synthesized 3-amino-p-anisyltetracetylglucose was converted to the corresponding benzoyl and p-toluenesulfonyl derivatives. Its diazotized product was subjected to azo coupling with aniline, phenol and β-naphtol.

EXPERIMENTAL

o-Anisyltetracetylglucose. A solution of 5 g (0.014 mole) of o-chlorotetracetylglucose in absolute ether was added to an ethereal solution of o-anisylmagnesiumbromide, obtained from 3.93 g (0.16 mole) of magnesium and 30.62 g (0.16 mole) of o-bromoanisole. The mixture was heated for 5 hours on a water bath; after it had cooled it was decomposed with water and dilute acetic acid. The aqueous layer was separated, evaporated to dryness under reduced pressure and was acetylated with 150 ml of acetic anhydride and 5 g of anhydrous sodium acetate. The reaction mixture was poured into cold water and was left until the excess acetic anhydride had completely decomposed. The solution was extracted with ether; the ethereal extract was washed with water and a solution of sodium bicarbonate; it was dried with calcined sodium sulfate and was decolorized with animal charcoal. After the evaporation of the ether 2.44 g (42% of the theoretical) of o-anisyltetracetylglucose in the form of a light transparent sirup was obtained.

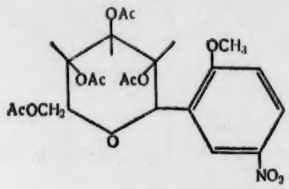
The substance was soluble in ether, methyl and ethyl alcohol and acetic acid; it was insoluble in water. o-Anisoic acid was obtained by destructive oxidation with alkaline permanganate. The substance is described for the first time.

Found % C 57.26; H 6.33 $C_{21}H_{26}O_{10}$. Calculated % C 57.53; H 5.99.

5-Nitro-2-methoxyphenyltetracetylglucose. 3 g of o-anisyltetracetylglucose in 16 ml of acetic anhydride and 10 ml of acetic acid were added dropwise with shaking over a period of 30 min to a solution of 13.2 g of copper nitrate trihydrate in 18.6 ml of acetic anhydride and 8 ml of acetic acid. The reaction mixture was heated on a water bath to 65-75°. After the completion of the reaction the mixture was poured into 400 ml of ice water with vigorous stirring. After half an hour the substance was extracted with ether; the ethereal extracts were washed with a solution of sodium bicarbonate and water and were then dried over calcium chloride. After the distillation of the ether 2.39 g (72.7% of the theoretical) of sirupy 5-nitro-2-methoxyphenyltetracetylglucose was obtained.

By means of destructive oxidation 5-nitro-2-methoxybenzoic acid was obtained and identified. As a result

of the analysis 3.24% nitrogen (calculated 2.89%) was found. The substance is described for the first time. Its structure is represented by the following formula:

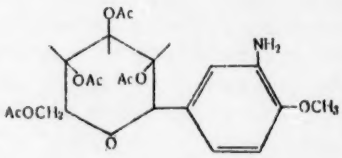


5-Bromo-2-methoxyphenyltetracetylglucose. A solution of 3.75 g (0.023 mole) of bromine in 10 ml of acetic acid was added to a solution of a 2 g (0.0046 mole) of o-anisyltetracetylglucose in 30 ml of glacial acetic acid. The mixture was left for an hour, after which it was poured into cold water. The reaction product was extracted with ether, the ethereal extracts were washed with a weak solution of alkali and water and were dried by anhydrous sodium sulfate. After the distillation of the ether 1.82 g (76.7% of the theoretical) of a sirupy product was obtained.

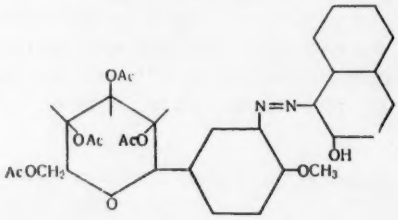
After recrystallization from isopropyl alcohol 5-bromo-2-methoxyphenyltetracetylglucose in the form of snow-white crystals with an m.p. of 147-148° was obtained. The product was readily soluble in the usual organic solvents. In the analysis for halogen 16.19% of bromine (calculated 15.47%) was found. The substance is described for the first time.

3-Amino-p-anisyltetracetylglucose. The 3-nitro-p-anisyltetracetylglucose, previously described [2], was reduced by hydrogen in the presence of Raney nickel, obtained by the usual method by treating an alloy containing 40% nickel with strong alkali.

1 g each of the indicated nitro compound and Raney nickel and also 40 ml of water were placed in a flask equipped with a mechanical stirrer. Hydrogen was passed from a Kipp's apparatus into the reaction mixture under the usual temperature and pressure conditions. The reduction was completed after 6-7 hours. The solution was filtered. The precipitate was recrystallized from a small amount of aqueous ethanol. The yield of the substance was 0.6 g (64% of the theoretical). The synthesized 3-amino-p-anisyltetracetylglucose was a cream-colored crystalline product with an m.p. of 154-157°. The result of a nitrogen determination by the Kjeldahl method was 3.15% (calculated 3.17%). The substance is described for the first time.



The presence of an amino group was confirmed by diazotization, followed by azo coupling. 0.1 g of the amine obtained was introduced into each of three test tubes and 3 ml of ethyl alcohol and a drop of hydrochloric acid were added to the tubes. The mixture was cooled to 5° and 2-3 drops of a sodium nitrite solution were then added to each of the test tubes. Several drops of aniline hydrochloride in water, phenol in alkali and β-naphthol in alkali, respectively were then added to the test tubes containing the diazo solution. In each case yellow-orange dyes were formed. In the latter case the structure is represented by the following formula:

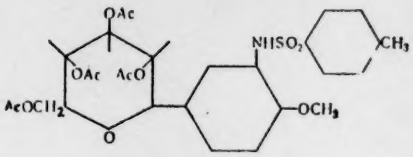


Benzoyl-3-amino-p-anisyltetracetylglucose. 0.2 g of the initial amine was dissolved in 5 ml of dry pyridine. A three-fold excess of benzoyl chloride (0.2 g) was added to the solution. The mixture was allowed to stand for 4 hours and was then poured into water. The precipitated product was filtered and recrystallized from ethyl alcohol. The yield was 0.1 g (41.6% of the theoretical).

The substance crystallized in the form of silvery plates with an m.p. of 162°. An analysis by the Kjeldahl method gave 2.36% nitrogen (calculated 2.38%). The substance is described for the first time.

3-Toluenesulfamino-p-anisyltetracetylglucose. 0.2 g of 3-amino-p-anisyltetracetylglucose was dissolved in 5 ml of dry pyridine. 0.2 g of p-toluenesulfonyl chloride was added to the solution obtained. After 4 hours the mixture was poured into water, of which a considerable excess was used. The precipitated product was filtered and recrystallized from ethyl alcohol. The yield was 0.11 g (41% of the theoretical).

The substance was crystallized in the form of white silvery plates with an m.p. of 161°. An analysis by the Kjeldahl method gave 2.41% nitrogen (calculated 2.41%). The substance is described for the first time. Its structure is represented by the following formula:



LITERATURE CITED

[1] Iu. A. Zhdanov. Prog. Chem., 25, No.9, 1165 (1956).

[2] Iu. A. Zhdanov, L. I. Shcherbakova, T. N. Egorova. Proc. Acad. Sci. USSR, 83, No. 3, 403 (1952).

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MOLECULAR HOMOGENEITY AND THE PROPERTIES OF CELLULOSE

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(Presented by Academician P. A. Rebinder June 3, 1958)

At one time the molecular weight of cellulose, as a high-molecular compound[1-4], was believed to be [5] about 500,000. Investigations on the retardation of the oxidative degradation of cellulose and viscosimetric measurements resulted in the figure for the molecular weight being increased [6-8] to nearly 1,600,000; this value was confirmed in recent works [9-11]. As far back as 1939 strange observations were reported which were difficult to explain [12-13]; the strength properties of natural cellulose fibers in the solid state are found at a mean molecular weight ($\overline{M}$) of about 32,000 and increase rapidly with increasing $\overline{M}$ to 113,000; with an increase of $\overline{M}$ to 160,000 the rise is increasingly less marked; further increase of $\overline{M}$ has no influence on the strength.

It was also established [14-15] that cellulose is heterogeneous along the length of the chain molecules. The indicated value of the molecular weight must, therefore, be considered as a mean value which definitely depends on the method of measurement.

A general representation of the heterogeneity of cellulose is given by the nonuniformity factor $\overline{U}$.

$$\overline{U} = \frac{\overline{M}_g}{\overline{M}_n} - 1,$$

where $\overline{M}_g$ and $\overline{M}_n$ are the mean gravimetric and mean numerical molecular weights, respectively. For homogeneous cellulose $\overline{U} = 0$.

In contemporary investigations the heterogeneity of cellulose is more fully and with greater mathematical accuracy described by the functions of integral and differential distribution [16].

At the present time individual attempts are being made to assess the variations in the heterogeneity by various processes of separation and treatment of cellulose and to link the heterogeneity with the quality of the cellulose and the properties of cellulose products. The principal result of these investigations is the recommendation to free cellulose from very short and very long chain molecules. The proposed assessment of the heterogeneity and its link with the mechanical properties of cellulose ester films, employing the factor of the shape of the mass distribution curve, is fairly complicated and offers little prospect of success.

We set ourselves the task of detailing more closely the problem of long chain molecules by clarifying the conceptions and the significance of the homogeneity of cellulose. According to our ideas the two following characteristics of homogeneity, obtained from the mass distribution curve are of decisive importance: the degree of homogeneity (monodispersion) influences the physical nature of the phenomenon, i.e. the predominant concentration of the substance near the maximum on the mass distribution curve ; this characteristic is described by the height and the base of the maximum on the curve. The second characteristic is determined by the value of the degree of polymerization (P), corresponding to the maximum.

The following considerations indicate the decisive importance of molecular homogeneity for the strength properties of artificial fibers. Chain molecules of cellulose having identical length will have an identical shape in solution. The viscosity of such a solution, homogeneous as regards its molecules, will be uniform in each elementary unit of the solution volume at different concentrations. In turn, the uniform viscosity of a spinning

solution ensures a high uniformity of orientation and a high uniformity of distribution of the molecules in the elementary fiber during the spinning process; this must result in a high value of the strength properties of the fiber. As is known, the high strength of a fiber is associated with the uniform distribution of the stress applied [17]. This uniform distribution acquires a limiting value in the case of a homogeneous fiber made from homogeneous cellulose.

From what has been said above it follows that the supramolecular structure of cellulose (the mutual disposition of the molecules and intramolecular bonds) must be determined by and may be regulated by the increase of the molecular homogeneity.

We employed the following method to make an experimental check of the ideas advanced. Using the precipitation method [18] to fractionate nitroesters obtained from the cellulose in finished articles (natural or artificial fibers, papers) and having decreasing strength properties, we were bound to obtain graphs of the mass distribution indicating a reduction in the molecular homogeneity.

From Curve 2, Fig. 1, it follows that a high rupture length of Meril fiber (54 km) corresponds to a high degree of homogeneity at P = 450. Curve 3, Fig. 1 indicates the considerable homogeneity of alkaline-chloro cellulose at P = 2800. Paper made from this cellulose has a high rupture length (9 km).

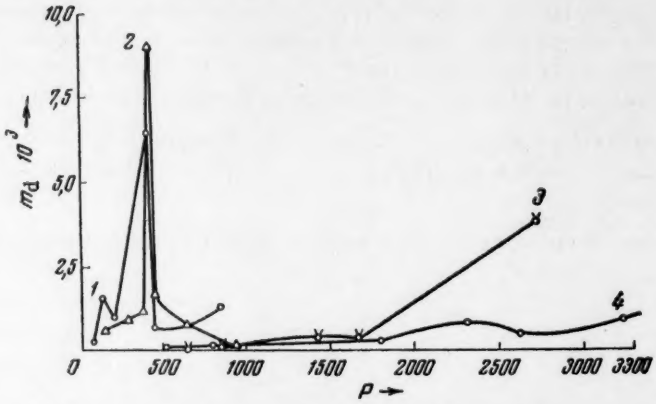

Fig. 1. Molecular homogeneity of cellulose, expressed as a function of a mass distribution $m_d = f(P)$. 1) Homogenization of alkaline-chloro cellulose by means of dilute nitric acid; 2) homogeneity of cellulose from artificial Meril fiber with a rupture length of 54 km; 3) homogeneity of wood cellulose obtained by the alkaline-chloro method (paper from this cellulose has a rupture length of 9 km); 4) heterogeneity of the initial cotton cellulose.

Our investigations showed the presence of a high degree of homogeneity in a number of celluloses at the following values of the degree of polymerization: Swedish cord celluloses 900-1200, Canadian cord cellulose 2,000 Soviet cellulose (sulfate cellulose upgraded by the IOKh method) 850. Siassk unbleached cellulose 2800. Cellulose acetate films have an average degree of homogeneity at P - 250.

The question quite naturally arises as to what methods are available for controllable variation of the heterogeneity of the molecular weight in order to obtain a high degree of homogeneity at a given value of the degree of polymerization. Our recalculations of the experimental data [19] on fractionation showed that hydrolysis with dilute hydrochloric acid and alkaline prematuration do not ensure the preparation of cellulose with a high degree of homogeneity.

We treated cotton cellulose, prepared according to Corey and Gray (its heterogeneity is shown by Curve 4, Fig. 1), with dilute nitric acid. As may be seen from Fig. 1 (Curve 1), cotton cellulose acquired a high degree of homogeneity at P = 400. The homogenization effect was also established with wood cellulose.

The results obtained are the first confirmation of the value of the homogeneity of cellulose for the strength properties and indicate one of the possible methods of obtaining the required homogeneity.

It must be assumed that molecular homogeneity is of great importance for the chemical and physical properties of cellulose and the behavior of natural and synthetic high-molecular compounds.

LITERATURE CITED

[1] B. Tollens, cited in Handbuch der Kohlenhydrate, Leipzig, 1914.

[2] E. Berl. R. Klaye, Z. ges. Schiess. u. Sprengstoff, 2, 381 (1907).

[3] H. Ost. Z. angew. Chem., 24, 1892 (1911).

[4] J. Boeseken, Rec. Trav. Chim., 35, 320 (1915).

[5] H. Staudinger, G. Daumiller, Lieb. Ann., 529, 219 (1937).

[6] O. P. Golova, I. I. Nikolaeva, Proc. Acad. Sci. USSR 29, 581 (1940).

[7] O. P. Golova, V. I. Ivanov. Bull. Acad. Sci. USSR, Div. Chem. Sci., 1945, 279.

[8] V. I. Ivanov, O. P. Golova, B. A. Zakharov. Bull. Acad. Sci. USSR, Div. Chem. Sci., 1950, 408.

[9] G. Meyerhoff, Naturwiss., 41, 13 (1954).

[10] M. Marx, Makromol. Chem., 16, 157 (1955).

[11] T. E. Timell, Svensk Papperstidn. 24, 836 (1957).

[12] H. Staudinger, J. Jurisch. Zellwolle, Kunstseide, Seide, 44, 375 (1939).

[13] H. Staudinger, J. Jurisch. Zellwolle, Kunstseide, Seide, 44, 377 (1939).

[14] H. Staudinger, Ber., 59, 3019 (1926).

[15] G. V. Schulz, Z. Elektrochem., 44, 102 (1938).

[16] V. I. Ivanov, B. A. Zakharov. Paper Ind., No. 2, 5 (1954).

[17] P. H. Hermans, Koll. Z.., 108, 177 (1944).

[18] R. L. Mitchell, Ind. and Eng. Chem., 45, 2526 (1953).

[19] Y. Siegwart, L. Rebenfeld, E. Pascu, Text. Res. J., 25, 1001 (1955).

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THE PREPARATION OF CARBON TETRACHLORIDE BY THE CHLORINATION OF METHANE IN A BOILING LAYER OF CATALYST

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M. M. Guseinov and F. A. Mekhtieva

Carbon tetrachloride is used as a solvent for oils, tars, paraffin and other organic substances; it serves as the initial material in the production of the cooling agent freon, enters into the composition of various fire-extinguishing agents and serves as the initial material for the synthesis of enanthic compounds. At present carbon tetrachloride is made principally by the method based on the chlorination of carbon bisulfide; this reaction is characterized by the complexity of the technological process and the fire hazard.

As far back as 1936 one of the authors of this article developed and tested on a semi-plant scale a method for obtaining carbon tetrachloride [2,3] by the catalytic chlorination of methane in the presence of carbon dioxide gas, acting as a diluent to eliminate the explosive nature of the reaction. For this purpose, the installations described in literature [4,5] provide for chlorination under conditions of formation of all the chloro derivatives of methane and stagewise chlorination.

Investigations in the field of the catalytic chlorination of alkanes, carried out up to the present time, have been based on the reaction taking place in the presence of an immobile layer of catalyst or fused salts. The work of A. V. Topchiev and his co-workers [6] on the chlorination of propane with a mobile contact catalyst forms an exception. Strictly speaking, the investigations of the last-mentioned authors cannot be included in the category of catalytic processes because the mobile contact catalyst is a fused stone, mullite, which acts as a chemically inert heat carrier.

The chain mechanism of the chlorination reaction of alkanes and its pronounced exothermic character exclude the possibility of reproducing it by a model, as a result of which serious complications occur when the process is carried out in large reactor systems. When the chlorination reaction is carried out with an excess of chlorine in the reaction mixture the reaction is accompanied by frequent explosions with the formation of soot which impairs the normal course of the reaction. To avoid the explosive nature of the chlorination reaction various authors have proposed diluting the reacting mixture with inert gases, i.e. nitrogen, hydrogen chloride, carbon dioxide, etc. Although the dilution of the reacting mixture with inert gases removes the danger of an explosion it creates additional difficulties associated with the condensation of the products of the diluted gas mixture, the circulation of inert gas, etc.

The most effective process for removing the above-mentioned shortcomings is to carry out the halogenation reaction in a boiling layer of finely-dispersed catalyst. When this process proposed by us is used, the chain reaction is retarded and its explosive development ceases as a result of the simultaneous impacts of the radicals and atoms against the particles of the catalyst powder.

In this connection we have carried out investigations on the preparation of carbon tetrachloride by the chlorination of natural gas in a boiling layer of catalyst within a wide range of variation of the parameters. Gas from the Duvanny deposit in the Azerbaidzhan SSR, containing 97-98% methane, served as the natural gas used in this investigation. The most active of the catalysts tested was found to be pumice and the data given refer, therefore, to this catalyst. The experiments were carried out in the apparatus represented in Fig. 1.

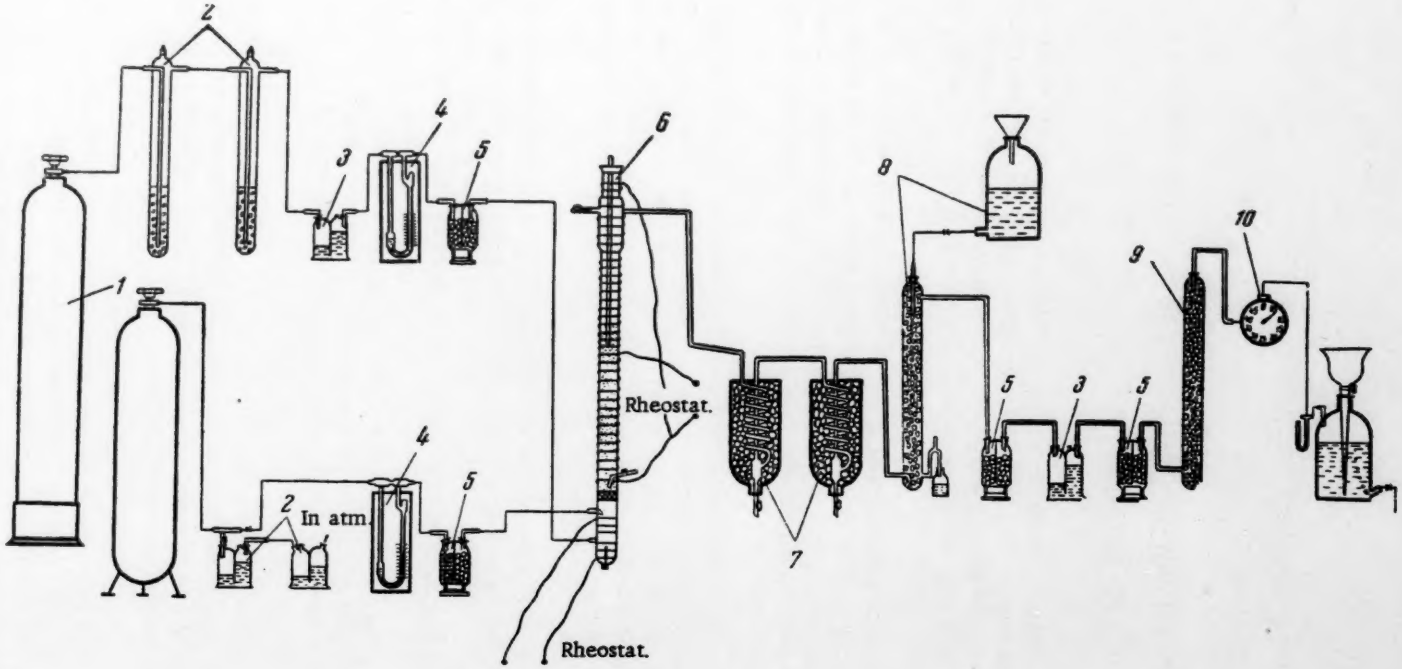

Fig. 1.

Natural gas from the cylinder 1, passing through the velocity regulator 2, the absorber containing sulfuric acid 3, the flow meter 4 and the calcium chloride flask 5, enters the lower part of the reactor 6 which functions as a mixer. The chlorine follows a similar path. The lower part of the reactor is separated from its main part by a glass filter. This filter acts as a regulator of the uniform feed of the mixture in the reaction zone and also removes the possibility of the catalyst entering the mixer.

The mixture of chlorine and methane passes through the filter into the reactor containing a boiling layer of catalyst powder. The reactor is a 3 cm diameter glass tube, 100 cm long, heated by means of an electrical winding. The temperature of the reactor is regulated by an automatic laboratory transformer and is measured by a thermometer located inside the reactor.

The reactor products enter the receiver-condenser 7, cooled by a mixture of ice and salt. To free the waste gases from hydrogen chloride they are passed through a column 8, sprayed with water. After passing through the calcium chloride flask the gases freed from hydrogen chloride pass into the carbon adsorber 9 to extract the uncondensed part of the reaction products and are collected in the gas tank 11.

TABLE 1

Characteristics of the experiments	Experiment No.				
	7	8	6	15	5
Experimental conditions					
Temperature, °C	380	400	420	380	410
Mol. ratio $CH_4 : Cl_2$	1 : 4	1 : 4	1 : 4	1 : 4	1 : 4
Velocity of CH_4, liters/hour	6,35	6,35	6,35	7,8	6,35
Velocity of Cl_2, liters/hour	25,4	25,4	25,4	31,1	25,4
Contact time, sec.	5,1	5,0	4,9	4,2	4,9
Duration of expt., hours	3,5	3,0	3,0	3,0	3,0
Used in the reaction (N.T.P.)					
CH_4	20,4	17,4	17,4	21,4	17,4
Cl_2	81,6	69,8	69,8	85,6	69,8
Obtained					
Catalyzate, g	140	96,4	79	142	109
HCL, g	132	104	125	140	113
Cl_2, g	2	20	25	2,4	8,0
Gas, liters	0,8	0,4	—	—	—
Properties of catalyzate					
d_4^{20}	1,6028	1,6028	1,6071	1,5905	1,5996
n_D^{20}	1,4608	1,4640	1,4650	1,4616	1,4618
Fractional Composition					
B.p.°C	59	72	72	59	63
Fraction 59—63°— yield %	0,2	—	—	1,7	—
Fraction 63—74°— yield %	6,4	1,6	5,2	8,8	6,6
d_4^{20}	1,5699	1,5710	1,5712	1,5695	1,5674
n_D^{20}	1,4582	1,4588	1,4589	1,4584	1,4580
Fraction 74—78° – yield %	85,8	88,5	83,6	82,0	86,5
d_4^{20}	1,5940	1,5932	1,5940	1,5942	1,5948
n_D^{20}	1,4615	1,4614	1,4613	1,4612	1,4626
Residue					
Yield, %	5,6	9,0	10,0	5,0	6,1
Losses, %	2,0	0,9	1,2	2,5	0,8
Material Balance with Respect to Cl, %					
In the catalyzate	49,0	41,0	33,0	48,2	45,4
In the formation of HCl	49,2	45,6	54,7	50,2	49,7
Free Cl_2	0,8	8,0	11,3	0,9	3,6
Losses	1,0	5,4	1,0	0,7	1,3

After the experiment the wash water was analyzed for the chlorine and hydrogen chloride contents and the catalyzate was investigated in detail. The results of typical experiments are given in Table 1.

As may be seen from the data in Table 1, at a temperature of 380-400°, a $Cl_2 : CH_4$ ratio of 4: 1 and a contact time of 5 sec in the boiling layer of finely-dispersed pumice, the chlorine completely takes part in the reaction, forming up to 90% carbon tetrachloride. The residue of 5-10% contains principally tetrachloroethylene and hexachloroethane.

The method developed for the synthesis of carbon tetrachloride by the chlorination of methane in a boiling layer of catalyst can also be used for the exhaustive chlorination of other alkanes

LITERATURE CITED*

[1] Iu. G. Mamedaliev. Symp. Sci. Trans. Azerbaidzhan SSR Petroleum Research Inst., Baku, 1936, p. 7.**

[2] Iu. G. Mamedaliev, A. M. Kuliev, Kh. A. Grigor'ian, A. B. Terterian. Trans. Div. Phys. Tech. Sciences and Petroleum, Acad. Sci. Azerb. SSR, 1, 102 (1953).

[3] W. Hirschkind, Ind. and Eng. Chem., 41, No. 12, 2749 (1949).

[5] L. F. Hatch, Petr. Refiner, 33, No. 12, 136 (1954).

[6] A. V. Topchiev and co-workers, Proc. Acad. Sci. USSR, 116, No. 5, 800 (1957).***

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THE TELOMERIZATION OF ETHYLENE WITH TETRACHLOROETHYLENE

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Chloroolefins, which cannot polymerize, can take part in a telomerization reaction with olefins. In this process the chloroolefins function as carriers of the chain reaction and supply end groups to the molecules of the telomers. Among reactions of this type the telomerization of ethylene with tetrachloroethylene is of conserable interest as a method of synthesizing reactive tetrachloroalkenes containing an even number of carbon atoms in the molecule (system (1)).

$$CCl_2 = CCl_2 + nCH_2 = CH_2 \xrightarrow{\text{initiator}} Cl\,(CH_2CH_2)_nCCl = CCl_2. \qquad (1)$$

It may be assumed that tetrachloroalkenes obtained by this method make it possible to synthesize various even-seried polyfunctional compounds similar to the manner in which various bi- and polyfunctional uneven-seried compounds are synthesized from $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes obtained by the telomerization of ethylene with carbon tetrachloride (for a summary of these reactions see [1]). It should be noted that compounds containing the $CCl_2{=}CCl$ group were previously difficultly obtainable; even their preparation from compounds containing the $CH{=}Cl_2$ group is a multistage process, for example, according to system (2):

$$RCH_2CCl_3 \rightarrow RCH = CCl_2 \rightarrow RCHCl\,CCl_3 \rightarrow RCCl = CCl_2. \qquad (2)$$

The telomerization reaction of ethylene with tetrachloroethylene should lead to the synthesis of compounds containing a trichlorovinyl group in one stage. This reaction is mentioned in the patent [2]. The reaction was carried out in the presence of benzoyl peroxide at 115° and 95 atm. Only tetrachlorohexene, boiling within a wide range of temperature, was isolated from the mixture of reaction products.

We carried out the reaction of ethylene with tetrachloroethylene under a pressure of 50 to 200 atm, with and without water; benzoyl peroxide, tertiary butyl peroxide, azodinitrile bis-isobutyric acid and azoaminobenzene were tried as initiators. In all instances there was a greater conversion of tetrachloroethylene when the reaction was carried out in water. Of the initiators tested the peroxides gave the best results.

The investigation showed that tetrachloroethylene is a less reactive carrier of the reaction chain than, for example, carbon tetrachloride or chloroform. For example, in the best experiments the conversion of tetrachloroethylene was only 20% provided that the initiator was repeatedly added during the reaction process. The inactivity of tetrachloroethylene is also indicated by the fact that the content of tetrachloroalkenes in the mixture of reaction products rises rapidly with increasing pressure. The fractionation of the mixture of reaction products showed that the lower $\alpha,\alpha,\beta,\omega$-tetrachloroalkenes (n = 1.2) are easily isolated in the individual form. The higher fractions contain by-products of the reaction which are difficult to remove. In spite of the difficulties indicated we succeeded in obtaining tetrachloroalkenes containing 4, 6 and 8 carbon atoms in the molecule and studying several chemical conversions of these compounds.

Diethylamino derivatives with the structure: $(C_2H_5)_2N(CH_2CH_2)_nCCl{=}CCl_2$, were obtained by the reaction of tetrachloroalkenes (n = 2.3) with diethylamine; this proves that only one chloromethyl group is present in the molecule.

Acetylene derivatives with the structure: $(C_2H_5)_2N(CH_2CH_2)_nC{\equiv}CH$, were obtained by the action of

metallic sodium on the bases obtained; this proves the presence of a trichlorovinyl group (comp. with [3]).

In contrast to the higher tetrachloroalkenes, as a result of reacting with diethylamine 1,1,2,4-tetrachloro-1-butene undergoes dehydrochlorination with the formation of 1,1,2-trichloro-1,3-butadiene.

EXPERIMENTAL

The telomerization reaction of tetrachloroethylene with ethylene. 1000 ml of tetrachloroethylene (1620 g), and 500 ml of water were added to a 2700 ml stainless steel rocking autoclave and ethylene was introduced up to a pressure of 50 atm. The mixture was heated to a temperature of 140°. At this temperature and pressure 20 ml of a solution of tertiary butyl peroxide in tetrachloroethylene was added every half hour. A total of 12 g of peroxide in 200 ml of tetrachloroethylene was added in 15 hours. The products from two experiments were combined, making a total of 4185 g of mixture. 2400 g of the mixture was fractionated.

After 1782 g of tetrachloroethylene had been distilled, a residue of 618 g was obtained which was fractionated under vacuum. The following were obtained: fraction I 35-65°/22 mm, 108 g; fraction II 60-90°/10 mm, 95 g; fraction III 90-115°/10 mm, 144 g; fraction IV 96-110°/2 mm, 50 g; fraction V 111-130°/2 mm, 27 g; fraction VI, residue of 173 g.

The following were obtained from fractions II, III and IV, respectively after redistillation in the column:

a) 1,1,2,4-Tetrachloro-1-butene (77g). B.p. 66°/9 mm, $n^{20}D$ 1.5140, d^{20}_4 1.4708. Found MR 39.69, Calculated MR for $C_4H_4Cl_4$ F 39.67.

Found % C 24.93; 24.98; H 2.17; 1.98. Calculated % C 24.77; H 2.08.

b) 1,1,2,6-Tetrachloro-1-hexene (130 g). B.p. 103-104°/8.5 mm, $n^{20}D$ 1.5090, d^{20}_4 1.3551. Found MR 48.92. Calculated MR for $C_6H_8Cl_4$ F 48.91.

Found %: C 32.67; 32.68; H 3.77; 3.79. Calculated % C 32.47; H 3.63.

Literature data [2]: b.p. 99-103°/10 mm, $n^{25}D$ 1.5060, d^{25} 1.3456.

c) 1,1,2,8-Tetrachloro-1-octene (27 g). B.p. 111-112°/2 mm, $n^{20}D$ 1.5060, d^{20}_4 1.2206. Found MR 58.26. Calculated MR for $C_8H_{12}Cl_4$ F 58.63.

Found % C 39.34; 39.40; H 4.68; 4.69. Calculated % C 38.43; H 4.83.

The intermediate fractions and the residue were not investigated.

1,1,2-Trichloro-1,3-butadiene. A solution of 90 g (0.46 mole) of 1,1,2,4-tetrachloro-1-butene in 67 g (0.92 mole) of diethylamine was added to three glass ampoules. The ampoules were heated to 22-25° and were kept at this temperature for 48 hours. The precipitated hydrochloride was separated, the solution was washed with a weak solution of acid, dried over sodium sulfate and distilled. 51 g (70.5% of the theoretical) of 1,1,2,-trichloro-1,3-butadiene was obtained with a b.p. of 75°/80 mm, $n^{20}D$ 1.5355, d^{20}_4 1.3733. Found MR 35.72. Calculated MR for $C_4H_3Cl_3$ F_2 34.34.

Found %: C 30.61; 30.25; H 2.15; 1.97; Calculated % C 30.51; H 1.92.

1,1,2,-Trichloro-1,3-butadiene readily polymerizes.

1,1,2-Trichloro-6-diethylamino-1-hexene. 44 g (0.2 mole) of 1,1,2,6-tetrachloro-1-hexene, 30 g (0.4 mole) of diethylamine and 50 ml of methyl alcohol were added to a stainless steel autoclave. The mixture was heated at a temperature of 95-105° for 6 hours and was treated in the usual manner. The base was dried over Na_2SO_4 and distilled. 43.2 g of 1,1,2-trichloro-6-diethylamino-1-hexene was obtained; the b.p. was 128.5°/9 mm, $n^{20}D$ 1.4860, d^{20}_4 1.1175. MR found 66.45. Calculated MR for $C_{10}H_{18}Cl_3N$ F 66.45.

Found % C 46.33; 46.42; H 7.88; 7.13. Calculated % C 46.44; H 7.02.

Hydrochloride, m.p. 187° (from alcohol).

Found % C 40.77; 40.79; H 6.63; 6.67. Calculated %: C 40.69; H 6.49.

1,1,2-Trichloro-8-diethylamino-1-octene. 95 g of a tetrachlorooctene fraction with a b.p. of 110-114°/

2 mm, 60 g (0.76 mole) of diethylamine and 50 ml of methyl alcohol were introduced into a stainless steel autoclave. The mixture was heated at 95-105° for 6 hours. After the usual treatment the basic products were separated from the neutral ones. The latter (15 g) were not investigated. As a result of the distillation of the basic products 28 g of 1,1,2-trichloro-8-diethylamino-1-octene was obtained; the b.p. was 147° / 5 mm, $n^{20}D$ 1.4855; d^{20}_4 1.0835. Found MR 75.90. Calculated MR for $Cl_2H_{22}NCl_3F$ 75.69.

Found % C 50.46; 50.56; H 7.82; 7.81. Calculated % C 50.27; H 7.73.

Hydrochloride, m.p. 116° (from acetone):

Found % C 44.83; 44.72; H 7.19; 7.19. Calculated % C 44.59; H 7.17.

6-Diethylamino-1-hexine. 7.84 g (0.34 mole) of metallic sodium, cut into small pieces, and 30 ml of ether were introduced in a three-neck flask and a small amount of 1,1,2-trichloro-6-diethylamino-1-hexene dissolved in ether was added with stirring. After 2-3 min the reaction commenced spontaneously and the remaining solution of 1,1,2-trichloro-6-diethylamino-1- hexene (a total of 21 g (0.085 mole) in 24 ml of ether) was then added dropwise. The thickened mass was stirred for 4 hours. After 15 hours the mixture was treated with methyl alcohol and water. The organic layer was extacted with ether, dried over Na_2SO_4 and distilled. 8.3 g of 6-diethyl-amino-1-hexine was obtained; the b.p. was 73° / 12 mm, $n^{20}D$ 1.4450, d^{20}_4 0.8120. Found MR 50.24. Calculated MR for $C_{10}H_{19}NF$ 50.31.

Found % C 77.83; 77.99; H 12.54; 12.47. Calculated % C 78.35; H 12.48.

Hydrochloride, m.p. 120.5-121° (from acetone):

Found % C 63.04; 62.82; H 10.60; 10.70. Calculated % C 63.30; H 10.62.

8-Diethylamino-1-octine. This was obtained from 40 g of 1,1,2-trichloro-8-diethylamino-1-hexene by treating it with metallic sodium in an ethereal solution as described in the preceding experiment. 15.5 g of 8-diethylamino-1-octine was obtained; the b.p. was 96° / 10 mm, $n^{20}D$ 1.4478, d^{20}_4 0.8146. Found MR 59.50. Calculated MR for $C_{12}H_{23}NF$ 59.54.

Found % C 79.14; 79.42; H 12.77; 12.90. Calculated % C 79.48; H 12.80.

Hydrochloride, m.p. 81° (from acetone).

Found % C 66.28; 66.36; H 11.17; 11.12. Calculated % C 66.17; H 11.10.

LITERATURE CITED

[1] A. N. Nesmeianov, R. KH. Freidlina, L. I. Zakharkin. Prog. Chem., 26, 655 (1956).

[2] U.S. Pat. 589065; Chem. Abstr., 42, 583 (1948).

[3] L. I. Zakharkin. Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, 1009.*

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THE SYNTHESIS OF ORGANOMERCURIC COMPOUNDS BY MEANS OF DIARYLIODONIUM SALTS

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As we have previously shown [1,2], the double salts of diaryliodonium chlorides and metallic chlorides can serve as a source for obtaining organometallic compounds of tin, antimony and bismuth. The reaction consists of the decomposition of double diaryliodonium salts by tin, antimony and bismuth powders as the case may be.

In the present paper the possibility of the extension of this reaction for the synthesis of organomercuric compounds is investigated. To find the optimum conditions we decomposed the double salt of diphenyliodonium chloride and mercuric chloride in various solvents, using a number of metals as reducing agents (Hg, Fe, Zn, Cu, Ag). The results of these experiment are given in Table 1.

Table 1

Yield of Organomercuric Compound (as a percentage) with Different Metals as Reducing Agents

Solvent	Reducing Agents				
	Hg	Fe	Zn	Cu	Ag
Water	70	–	–	–	–
Acetone	34	3(39)*	30	16	0
Ethyl alcohol	–	5(21)*	Traces	9	–

* Yield of mercury diphenyl indicated in brackets.

As may be seen from Fig. 1, when iron was used as the reducing agent, the principal reaction product was mercury diphenyl, while in the other instances it was C_6H_5HgCl. Silver decomposes the double salt $(C_6H_5)_6ICl \cdot HgCl_2$ with the formation of diphenyliodonium chloride and calomel; organomercuric compounds are not formed in this reaction. The maximum yield of phenylmercuric-chloride is obtained by the decomposition of the double salt of diphenyliodonium chloride and mercuric chloride by mercury in water

$$(C_6H_5)_2ICl \cdot HgCl_2 + Hg \rightarrow C_6H_5HgCl + C_6H_5I + HgCl_2.$$

The decomposition of $(p\text{-}ClC_6H_4)_2ICl \cdot HgCl_2$ and $(p\text{-}CH_3OC_6H_4)_2ICl \cdot HgCl_2$ under similar conditions led to the formation of p-chlorophenylmercurochloride (yield 45%) and p-anisylmercuric chloride (yield 28%), respectively.

Organomercuric compounds are, therefore, only obtained with a high yield from double diaryliodonium salts of mercuric chloride in the case of $(C_6H_5)_2ICl \cdot HgCl_2$. In addition, in the synthesis of organomercuric compounds from Ar_2ICl $HgCl_2$ the initial diaryliodonium salts must first be obtained; in a number of instances the latter are formed with difficulty because of the low solubility of Ar_2ICl. This fact is a particularly serious obstacle to wide-scale use of diaryliodonium salts of $HgCl_2$ for the synthesis of organomercuric compounds. We, therefore, subsequently decided to use diphenyliodonium salts directly as the initial substances for the preparation of organometallic compounds of mercury.

There are indications in literature of the use of diaryliodonium salts for the synthesis of organometallic compounds. For example, Sandin, McClure and Irwin [3] obtained C_6H_5HgCl and $p\text{-}CH_3C_6H_4HgCl$ by the decomposition of the chlorides of the corresponding diaryliodoniums by mercury in boiling propyl alcohol. The yield was only given for phenylmercuric chloride (40%). When L. G. Makarova and A. N. Nesmeianov [4] repeated the experiment of Sandin and his co-workers they obtained a 50% yield of C_6H_5HgCl.

TABLE 2

Solvent	Yield of C_6H_5HgCl, %
Acetone	76
Benzene	50
Water	34
Propyl alcohol [3]	40

TABLE 3

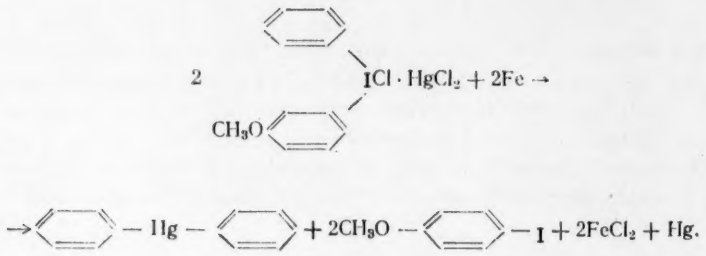
Initial diaryl-iodonium salt	Reaction product	Yield, %
$(C_6H_5)_2$ ICl	C_6H_5HgCl	76
$(p\text{-}CH_3C_6H_4)_2$ ICl	$p\text{-}CH_3C_6H_4HgCl$	55
$(p\text{-}CH_3O(C_6H_4)_2$ ICl	$p\text{-}CH_3OC_6H_4HgCl$	53
$(p\text{-}ClC_6H_4)_2$ ICl	$p\text{-}ClC_6H_4HgCl$	77
$(p\text{-}BrC_6H_4)_2$ ICl	$p\text{-}BrC_6H_4HgCl$	75
$(m\text{-}O_2NC_6H_4)_2$ ICl	$mO_2NC_6H_4HgCl$	40
$(m\text{-}C_2H_5OCOC_6H_4)_2$ ICl	$mC_2H_5OCOC_6H_4HgCl$	47

Because of the fact that the scanty data available at present on the use of diaryliodonium salts for the preparation of organometallic compounds are only of an approximate character we undertook a detailed investigation of the possibility of synthesizing organometallic compounds from diaryliodonium salts. The results of the decomposition of diphenyliodonium chloride by metallic mercury in various solvents are given in Table 2.

As may be seen from Table 2, the most favorable solvent is acetone, in which the reaction was usually carried out in the following manner. Diaryliodonium chloride (0.01 mole) was stirred vigorously with 2 ml of mercury in 100 ml of acetone for 3 hours at 56°. The precipitate was filtered, extracted with acetone and the extract was combined with the filtrate. The solution obtained was evaporated. The organomercuric compound remaining was freed from the corresponding iodine derivative formed during the reaction process by washing with hot petroleum ether. After recrystallization the analytically pure organomercuric compound was obtained. The compounds synthesized by the above method are given in Table 3.

As may be seen from Table 3, good yields of organomercuric compounds are obtained from diaryliodonium salts. This fact, together with the simplicity of carrying out the synthesis and the comparative readiness with which diaryliodonium salts are obtained justify the consideration that the proposed method of synthesis is a convenient means of obtaining organomercuric compounds.

It should be mentioned that in addition to symmetrical diaryliodonium salts we decomposed three unsymmetrical salts $C_6H_5(p\text{-}CH_3OC_6H_4)ICl$, $(p\text{-}CH_3OC_6H_4)(p\text{-}C_2H_5OCOC_6H_4)ICl$ and $C_6H_5(p\text{-}IC_6H_4)ICl$. In the first two instances C_6H_5HgCl (yield 70%) and $p\text{-}C_2H_5OCOC_6H_4HgCl$ (yield 56%) were obtained, respectively, i.e. of the two radicals the more electronegative one was converted to mercury. We also noted the conversion of the more electronegative radical in the decomposition of the double salt of $C_6H_5(p\text{-}CH_3OC_6H_4)ICl \cdot HgCl_2$ by iron dust. Here, as in the case of the decomposition of the double salt of diphenyliodonium chloride and mercuric chloride the main product was mercury diphenyl (yield 29%) together with traces of phenylmercuric chloride. The decomposition of $C_6H_5(p\text{-}IC_6H_4)ICl$ by mercury however, leads to the formation of a mixture of products: C_6H_5HgCl and $p\text{-}IC_6H_4HgCl$, i.e. in this instance both radicals are converted to mercury. This is probably explained by the fact that the difference in the electronegativity of the phenyl and p-iodophenyl radicals is not so great as in the two previous instances.



LITERATURE CITED

[1] O. A. Ptitsyna, O. A. Reutov, M. F. Turchinskii. Proc. Acad. Sci. USSR, 114, 110 (1957).*

*Original Russian pagination. See C. B. Translation.

[2] O. A. Reutov, O. A. Ptitsyna, G. Ertel, Chem. Techn., No. 4, 201 (1958).

[3] R. Sandin, F. McClure, F. Irwin, J. Am. Chem. Soc., 61, 2944 (1939).

[4] L. G. Makarova, A. N. Nesmeianov, Bull. Acad. Sci. USSR, Div. Tech. Sci., 1945, 617.

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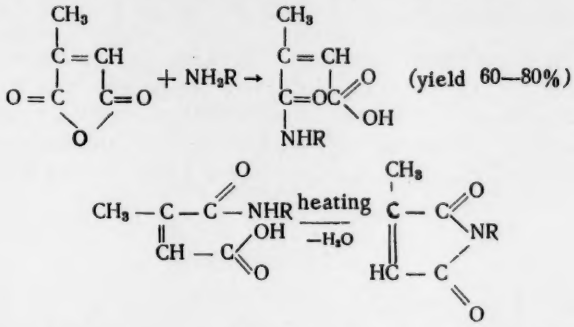
A NEW METHOD OF OBTAINING N-METHYL CITRACONIMIDE

T. V. Sheremeteva and T. A. Trushkova

(Presented by Academician B. A. Kazanskii May 16, 1958)

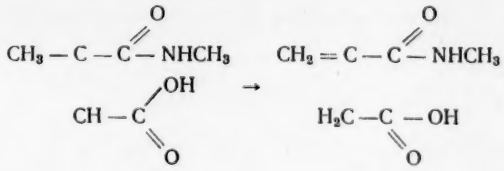
As was shown by one of the authors [1] the synthesis of previously undescribed alkyl citraconimides can be accomplished in a similar way to the synthesis of alkyl maleinimides developed by Piutti [2] in the 19th century.

The reaction takes place in two stages according to the following system:

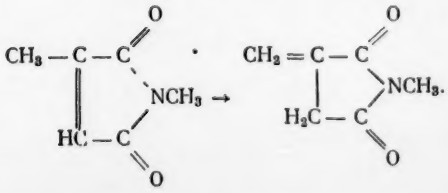


In our first experiments at a dehydration temperature of 160-200°, i.e. under the conditions selected by Piutti for preparing alkyl maleinimides, the formation of alkyl citraconimides was accompanied by considerable tarring and their yield did not exceed 40% of the theoretical, calculated on the amido acid consumed and was, therefore, 24-32% of the citraconic anhydride. The reduction of the reaction temperature to 130-140° made it possible to reduce tarring and increase the yield of imides to 50-75% of the amido acid and, therefore, to 37-50% of the anhydride.

We explained the formation of considerable tarring by the isomerization of the alkyl amides or alkyl imides of citraconic acid to the corresponding derivatives of itaconic acid.



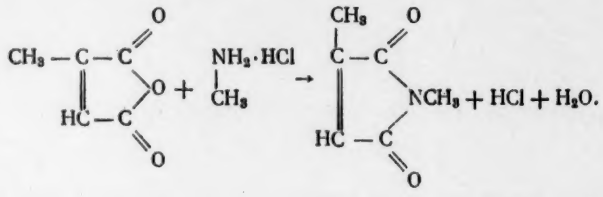
or



Derivatives of itaconic acid, being representatives of unsymmetrically substituted ethylene, tend to polymerize, i.e. to form tar.

In 1899 Fittig [3] showed that an alkaline medium assists the isomerization of citraconic acid to itaconic acid. In the dehydration of an alkyl amide an alkaline medium may appear as a result of partial thermal decomposition with the formation of free alkylamines.

In order to remove this phenomenon, in addition to the reduction of the reaction temperature, experiments were carrried out on obtaining methyl citraconimide by the action of methylamine hydrochloride on citraconic anhydride.



The hydrogen chloride liberated during the reaction assisted the dehydration and produced an acid medium for the reaction mixture which ensured the elimination of isomerization. In this instance the yield of N-methyl citraconimide varied from 70-80% of the anhydride, instead of 36-50% by the first method.

In order to confirm the hypothesis advanced, i.e. that in the above-mentioned reaction an acid medium eliminates the isomerization of derivatives of citraconic acid into the corresponding derivatives of itaconic acid, an experiment was carried out to obtain N-methyl itaconimide by reacting methylamine hydrochloride with itaconic anhydride. As a result of the reaction 40% of the theoretically possible yield of N-methyl citraconimide was obtained; the remaining part of the reaction mixture tarred up. We did not succeed in isolating N-methyl itaconimide.

EXPERIMENTAL

Equimolecular amounts of citraconic anhydride and methylamine hydrochloride were mixed in a Wurtz flask having two tubes. The flask was connected to a Liebig condenser (descensional type) and was equipped with two thermometers for measuring the temperature of the reaction mixture and the vapors as well as a barometer for the inert gas. Heating was carried out on an oil bath or in Wood's alloy. The temperature of the reaction mixture was kept at 130-140° for 8 hours and at 160-200° for 2 hours with constant bubbling of CO_2 or nitrogen. During this process the main mass of the reaction water and HCl distilled over and in the last 2 hours a small amount of imide was distilled.

On the completion of heating, the condenser was connected with a receiver connected to a water-jet pump and the entire reaction mass was distilled without fractionation at a residual pressure of 30-40 mm.

After the distillate had been neutralized with soda the imide was extracted with ether. The ethereal extract was dried with Na_2SO_4. The ether was distilled off and the imide was distilled under vacuum.

The results of the experiments are given in Table 1.

An experiment was carried out to obtain N-metyl itaconimide.

The initial products were 5.6 g (0.05 mole) of itaconic anhydride and 3.4 g (0.05 mole) of methylamine hydrochloride.

As a result of the reaction 2.5 g of a liquid product was obtained; the b.p. was 84.5-85°/10 mm, the specific gravity was 1.1530 and the coefficient of refraction 1.4943.

All the constants of this compound correspond to the constants of N-methyl citraconimide.

Found %: C 57.68; H 5.5; N 11.5. $C_6H_7NO_2$. Calculated %: C 57.60; H 5.6; N 11.2.

(The reaction was accompanied by considerable tarring).

TABLE 1

Amt. of citraconic anhydride		Amt. of CH_3NH_2HCl		Yield			Refractive index *
g	Mole	g	Mole	g	Mole	%	
22,4	0,2	13,5	0,2	19,05	0,1524	76,2	1,4938
112	1	70	1,03	93,3	0,748	74,8	1,4940
42,4	0,38	25,7	0,38	37,3	0,30	78,8	1,4938
22,4	0,2	13,5	0,2	17,8	0,143	71,5	1,4940

The refractive index of N-methyl citraconimide was previously determined by us as 1.4942.

In the reaction of itaconic anhydride with methylamine hydrochloride isomerization takes place with the formation of N-methyl citraconimide, the yield of which is 40% of the theoretical.

LITERATURE CITED

[1] T. V. Sheremeteva, G. N. Larina. Bull. Acad. Sci. USSR, Div. Tech. Sci. (in press). *

[2] A. Piutti, E. Giustiniani, Gazz.Chim. Ital., 26, parte I, 431 (1896).

[3] R. Fittig, Lieb Ann., 304, 155 (1899).

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THE LIMITED APPLICABILITY OF THE AUWERS-SKITA RULE TO STEREOISOMERIC DIALKYLCYCLOALKANES

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I. M. Kuznetsova

In recent years we have noticed more than once that the Auwers-Skita rule (according to which trans-dialkylcycloalkanes have lower boiling points, lower refractive indices and densities, and higher molar refractions than cis isomers) does not apply to 1,3-dialkylcyclopentanes and 1,3-dialkylcyclohexanes, for in these series the relationships between the properties of cis- and trans-isomers become reversed. In the case of stereoisomeric 1,3-dimethylcyclopentanes and 1,3-dimethylcyclohexanes this was confirmed with thermodynamic data and synthesis.

We have recently observed a case where in a series of 1,4-dialkylcyclohexanes a singular divergence from this rule also takes place [1]; until now no one has disputed the applicability of the Auwers-Skita rule to these isomers. We discovered that in the case of stereoisomeric 1,4-diisopropylcyclohexanes, density and refractive index were higher, molar refraction and melting point lower* for the low-boiling isomer (which on the basis of spectroscopic data was cis). Thus, in the case studied by us not the trans-but the cis-isomer was the low-boiling one-contrary to the Auwers-Skita rule.

We show in this paper that the facts so far accumulated could provide a new approach to the interdependence of configuration and physical constants; we also show that applicability of the Auwers-Skita rule is obviously limited by the position of side chains in dialkylcycloalkanes as well as by the number of carbon atoms in the molecule.

We have already observed [2] that the boiling points, refractive indices, and densities of each isomeric pair in the 1,4-dialkylcyclohexane series get closer with increase in the hydrocarbon molecular weight. When molecular weights of dialkylcycloalkanes increase, the constants of the trans-isomer increase faster than those of cis-isomer, with a resulting approach in values. Of course, a faster increase in the constants of one isomer creates a possibility that at some molecular weight of the hydrocarbon one of the trans constants (for example boiling point) though usually lower, may become higher than the corresponding one of the cis-isomer. Thus, if we plot the values of $\Delta t = t_c - t_t$, where t_c and t_t are the boiling points (at 760 mm) of cis-and trans-isomers respectively, then we can show that the differences obtained fall on a straight line (see Table 1 and Fig. 1, Line C). Around C_{11} this line intersects the abcissa; consequently, cis-1,4-dialkylcyclohexanes with more than 11 carbons atoms should boil below the trans-isomers. It seems that it was this phenomenon that we encountered in the case of stereoisomeric 1,4-diisopropylcyclohexanes.

Hence, the reversal in relative boiling points of stereoisomeric 1,4-diisopropylcyclohexanes (reversal of what the Auwers-Skita rule would predict)seems to be a regular phenomenon. On the other hand, the values of refractive indices and densities remain higher in the cis-isomer of this hydrocarbon. Apparently the lines representing the functions of corresponding differences (Δn and Δd)did not yet intersect the abcissa. Let us note by the way, that lacking sufficient experimental data we can not at the present time make a precise deduction about the geometrical form of Δn and Δd as a function of the number of carbon atoms in the molecule. Still, the available information shows that these constants also get closer with increase in the molecular weight of stereoisomeric 1,4-dialkylcyclohexanes (Table 1).

* In the series of 1,4-disubstituted cyclohexanes a higher melting point is characteristic for the trans-form.

TABLE 1

The Properties of Cis-and Trans-1,4-dialkylcyclohexanes.

Hydrocarbon	B.P. in °C at 760 mm			n_D^{20}			d_4^{20}		
	Cis	Trans	Difference	Cis	Trans.	Difference	Cis	Trans.	Difference
1,4-Dimethylcyclohexane [3]	124,321	119,351	4,970	1,42966	1,42090	0,00876	0,78285	0,76255	0,02030
1-Methyl-3-ethylcyclohexane [2]	152,6	149,1	3,5	1,4374	1,4304	0,0070	0,7969	0,7798	0,0171
1-Methyl-4-isopropylcyclohexane [4]	172,7	170,5	2,2	—	—	—	—	—	—
1,4-Diisopropylcyclohexane [1].	215,1*	217,1*	−2,0	1,4524	1,4485	0,0039	0,8236	0,8143	0,0093

* The boiling point was determined in vacuo, and the value listed here was calculated using Dreisbach's tables [5].

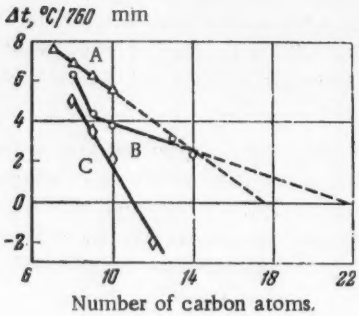

Fig. 1. The difference in boiling point between stereoisomers as a function of numer of carbon atoms in the molecule. 1) Line A = 1,2-Dialkylcyclopentanes; 2) Line B = 1,2-dialkylcyclohexanes; 3) Line C = 1,4-dialkylcyclohexanes.

From the comparisons made above we can conclude that stereoisomeric 1,4-dialkylcyclohexanes with 12 or more carbon atoms in the molecule should deviate from the investigated rule similarly to 1,4-diisopropylcyclohexanes; i.e. the cis configuration, which probably shall possess a higher ($n^{20}D$ and d^{20}_4, will represent the low-boiling isomer. At an even larger molecular weight, we do not exclude the existance of trans-isomers with refractive indices and densities greater than those of cis-isomers. Therefore, we can presume that the applicability of the Auwers-Skita rule is limited only to the first few members of the 1,4--dialkylcyclohexane series.

The fact that stereoisomers with various side chains (methyl, ethyl, isopropyl) show a direct dependence between the boiling point differences and the number of carbons in the molecule is very remarkable. It seems to indicate, that for a given number of carbon atoms in any one series the values of Δt should be similar among isomeric cycloalkanes with different radicals.

A literature search and our own data on the boiling points of stereoisomeric cycloalkanes showed that a linear dependence of Δt on the number of carbon atoms in the molecule is not exclusively limited to 1,4-dimethylcyclohexanes. Actually, Table 2 and Line A in Fig. 1 show that in the 1,2-dialkylcyclopentane series the differences between the boiling points of stereoisomers also fit pretty well on a straight line. In the case of 1,2-dialkylcyclohexanes (Table 3 and Fig. 1, Line B) the first member of the series (1,2-dimethylcyclohexane) does not fall on the line, while the remaining known members give a fully satisfactory straight line. However, in the case of these two series the slopes of the lines are much less steep than in the case of 1,4-dialkylcyclohexanes, and therefore the intersection with the abcissa – if it occurs at all – would be expected only among hydrocarbons having 18 and 22 carbon atoms respectively. Among stereoisomeric 1,2-dialkylcycloalkanes investigated, the boiling points of the trans-isomers also increase faster with increase in the molecular weight than do those of cis-isomers; yet in these cases the Auwers-Skita rule should have a slightly wider applicability than in the case of 1,4-dialkylcyclohexanes.

It should be noted that the literature contains data [10] on the stereoisomers of 1-methyl-4-tertbutylcyclohexanes, for which the boiling point difference is 2 (or -2, in as far as the geometrical configuration of the stereoisomers has not been established) instead of a value close to zero as expected for C_{11}. It is possible that this exception to the linearity is connected with the large size of a tert-butyl group.

As a conclusion it should be emphasized that until supplementary data appears we cannot exclude the possibility that in all the cases investigated Δt is not a linear function of molecular weight, but lies on a curve

TABLE 2

The Properties of Cis-and Trans-1,2-dialkylcyclopentanes

Hydrocarbon	B.p. in °C at 760 mm			n_D^{20}			d_4^{20}		
	Cis	Trans	Difference	Cis	Trans	Difference	Cis	Trans	Difference
1,2-Dimethylcyclopentane [3]	99,532	91,869	7,663	1,42217	1,41200	0,01017	0,77262	0,75144	0,02118
1-Methyl-2-ethylcyclopentane[3]	128,050	121,2	6,8	1,42933	1,4219	0,0074	0,78522	0,7690	0,0162
1-Methyl-3-n-propylcyclopentane [6]	152,58	146,37	6,21	1,43442*	1,42750*	0,0069	0,7921	0,7774	0,0147
1-Methyl-2-n-butylcyclopentane [7]	174,5	169,0	5,5	1,4381	1,4321	0,0060	0,7980	0,7847	0,0133

* For the yellow He line.

TABLE 3

Properties of Cis-and Trans-1,2-dimethylcyclohexanes

Hydrocarbon	B.p. in °C at 760 mm			n_D^{20}			d_4^{20}		
	Cis	Trans	Difference	Cis	Trans.	Difference	Cis	Trans	Difference
1,2-Dimethylcyclohexane [3]	129,728	123,419	6,309	1,43596	1,42695	0,00901	0,79627	0,77601	0,02026
1-Methyl-2-ethylcyclohexane [8]*	155,97	151,69	4,28	1,4432	1,4382	0,0050	0,8094	0,7972	0,0122
1-Methyl-2-n-propylcyclohexane [9]	175,9**	172,1**	3,8	1,4460	1,4408	0,0052	0,8127	0,7997	0,0130
1-Methyl-2-n-hexylcyclohexane [9]	242,6**	239,4**	3,2	1,4527	1,4490	0,0037	0,8208	0,8116	0,0092
1-Methyl-2-n-heptylcyclohexane [9]	260,5**	258,1**	2,4	1,4540	1,4503	0,0027	0,8229	0,8143	0,0086

* At the same time as authors of [8], we synthesized and separated into stereoisomers 1-methyl-2-ethylcyclohexane. With the exception of the cis-isomer density, the constants obtained by us are practically the same as the ones listed in Table 3 (for the cis-isomer: b.p. 156.05° at 760 mm, $n^{20}D$ 1.4432, d^{20}_4 0.8106; for the trans: b.p. 151.75° at 760 mm, $n^{20}D$ 1.4383, d^{20}_4 0.7970).

** The boiling point was determined in vacuo, and the value listed here was computed using Dreisbach's tables.

with large curvature (for example on the linear part of a hyperbola). Actually it would be hard to admit that differences between boiling points of stereoisomers could increase to indefinitely large numbers. One would rather think, that beginning with some number of carbons in the molecule the values of Δt would change slower than expected from the straight line or quit changing at all. However, this discussion should in no way reflect on the primary conclusion of this work concerning the conditionality and limited applicability of the Auwers-Skita rule.

LITERATURE CITED

[1] A. L. Liberman, T. V. Lapshina, B. A. Kazanskii, Proc. Acad. Sci. USSR, 107, 93 (1956).*

[2] B. A. Kazanskii, A. L. Liberman, Proc. Acad. Sci. USSR, 101, 877 (1955).

[3] F. D. Rossini et al., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Pittsburgh, 1953.

[4] F. D. Rossini, B. J. Mair, A. J. Streiff, Petroleum Hydrocarbons [In Russian], L., 1957, p. 83.**

*Original Russian pagination. See C. B. Translation.

**Russian translation.

[5] R. R. Dreisbach, Pressure-Volume-Temperature Relationships of Organic Compounds, Ohio, 1952.

[6] G. Chiurdoglu, Bull. Soc. Chim. Belg., 42, 347 (1933); 43, 35 (1934); 44,527(1935);Bull.Acad.Roy.Belg. Cl. Sci. (5), 17, 1404 (1931).

[7] A. F. Plate, A. L. Liberman, N. A. Momma, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 689.

[8] S. F. Birch, R. A. Dean, E. V. Whitehead, J. Org. Chem., 19, 1449 (1954).

[9] A. L. Liberman, I. M. Kuznetsova, N. I. Tiun'kina, B. A. Kazanskii, Proc. Acad. Sci. USSR, 118, 942 (1958).*

[10] K. T. Serijan, P. H. Wise, L. C. Gibbons, J. Am. Chem. Soc., 71, 2265 (1949).

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POLAROGRAPHIC REDUCTION OF SOME AROMATIC SANDWICH COMPOUNDS OF CHROMIUM

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While the polarographic behavior of bis-cyclopentadiene compounds is described with enough details [1], there is only one paper [2] on the reduction of $[(C_6H_6)_2Cr]^+$ cation using a mercury drop electrode in a nonaqueous solution of $CH_3OH + C_6H_6$ with sodium hydroxide, lithium chloride, or mixed solution of the latter with acetic acid used as supporting electrolytes.

Since we had prepared in our own laboratory the iodides of dibenzene-(I), ditoluene-(II), dimesitylene-(III), and bisdiphenylchromium (IV), as well as previously undescribed iodides of dicumene-(V) and di-(cyclohexylbenzene)- chromium (VI), it seemed worth our while to investigate the polarographic reduction of this series of compounds.

To synthesize the above mentioned derivatives (I) - (VI) we used a reduction reaction (the Friedel-Krafts reaction [3]). A mixture containing 23.8 g of anhydrous $CrCl_3$ (0.15 moles), 2.7 g of powdered aluminum (0.10 g-at.), 16 g of freshly redistilled $AlCl_3$ (0.11 moles), and 75 ml of cumene was boiled with stirring for 2 hours under a nitrogen atmosphere; during cooling it was hydrolyzed first with methanol, then with water. Surplus cumene was washed away with cyclohexane, while the aluminum and chromium hydroxides were precipitated with concentrated NH_4OH solution. After warming it up to 60° we filtered out the precipitate and washed it three times with small portions of warm water. To the filtrate we added an equal volume of benzene, a saturated solution of 35 g of sodium dithionate, flushed the flask with nitrogen, and gradually introduced a 60 g solution of concentrated potassium hydroxide. On the following day the aqueous layer was separated and discarded. To the dark-orange benzene layer we added 100 ml of water and bubbled air through the system. We settled out compound (V) in the form of a cherry-red viscous oil by adding a saturated aqueous solution of KI to the concentrated solution of dicumenechromium hydroxide obtained above. An effort to crystallize (V) was unsuccessful.

Found % Cr 12.39; I 30.33. $C_{18}H_{24}CrI$. Calculated % Cr 12.41: I 30.31.

Compound (V) is quite soluble in lower alcohols, acetone, methylene chloride, dichloroethane, pyridine, dimethylformamide, practically insoluble in ether, CCl_4, cyclohexane, water, and benzene. Compound (VI) was synthesized in a similar fashion. The reaction mixture, to which 50 ml of purified n-nonane was added, was heated for 1.5 hours at 150°. Compound (VI) precipitated as a dark-red colored powder.

Found % Cr 10.37; I 25.50. $C_{24}H_{32}CrI$. Calculated % Cr 10.42; I 25.45.

The solubility of (VI) is the same as that of (V).

Polarographic investigations of iodides (I) - (VI) were carried out on a visual polarograph issued by the Gorki Sci. Res. Institute of Chemistry. A capillary for which $m^{2/3}\ \tau^{1/6}$ was 1.16 mg $^{2/3}$ · sec.$^{-1/2}$ with an interrupted circuit was used as an electrode. A saturated calomel half cell was used as an anode relative to which the half-wave potentials were measured.

The reduction was conducted with various 0.5 N aqueous supporting electrolytes: lithium chloride, sodium hydroxide, potassium nitrate, sodium sulfate, hydrochloric acid, and buffered solutions between pH 2.3 and 11.75.

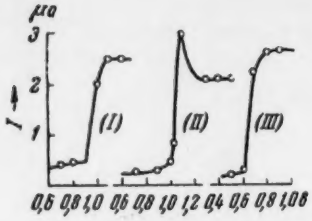

Fig. 1. Reduction waves with 0.5 N LiCl as supporting electrolyte.

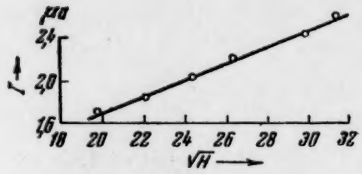

Fig. 2. The diffusion current as a function of the square root of mercury column for compound (IV).

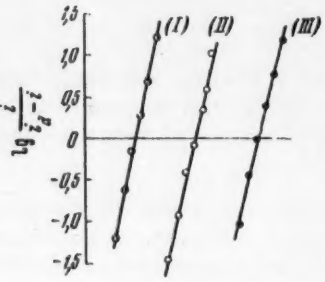

Fig. 3. The potential as a function of $\lg \frac{i}{i_d - i}$

Aromatic compounds of chromium gave diffusion currents in almost all the above mentioned electrolytes; the exceptions were, 0.5 N hydrochloric acid and buffered solutions with pH < 2, in which the compounds precipitated or (for example (II)) did not give reduction waves. All the iodides (I) - (VI) show one-wave reduction (Fig. 1) the limiting current of which has a diffusion character since its magnitude is proportional to the square root of the height of a mercury column (Fig. 2). With compounds (II), (III), (V), and (VI) a maximum was observed on the wave, but it could easily be suppressed with a solution of joiner's glue. In all the aromatic chromium compounds investigated, a direct proportion between reduction current and concentration was observed.

The half-wave potential of each compound does not depend on the nature of supporting electrolyte nor on the hydrogen ion concentration, but is displaced when the bonded aromatic rings are substituted. Thus, we obtained the following half-wave potentials, $E_{1/2}$ (in volts) for aromatic chromium compounds with 0.5 N LiCl as supporting electrolyte:

(IV) – 0.66	(I) – 0.97
(VI) – 0.9	(II – 1.04
(V) – 0.96	(III) – 1.06

Analysis of individual polarograms of aromatic chromium compounds showed that there is a linear relationship between half-wave potential and quantity $\lg \frac{i}{i_d - i}$ (Fig. 3); this corresponds to the Heyrovsky-Ilkovic equation:

$$\pi = \pi_{1/2} - \frac{0,058}{n} \lg \frac{i}{i_d - i},$$

where $\pi_{1/2}$ = the half-wave potential, i_d = limiting diffusion current, n = number of electrons involved in the electrode reaction. For the compounds we studied, n was 1; this we determined graphically and by the method of polarographic coulometry [4]. Conformity with the Heyrovsky-Ilkovic equation would indicate that a reversible reduction process takes place on the mercury drop electrode. This has also been observed when $[(C_6H_6)_2Cr]^{+}$ was reduced in an nonaqueous medium [2]. Consequently the reduction mechanism consists of a union between an electron and a cation of bisarene chromium compound:

$$(\text{Arene})_2\,Cr^+ + e \rightleftarrows (\text{Arene})_2\,Cr^0.$$

Studying the data obtained, we can conclude that introduction of an alkyl (V) or cyclohexyl(VI) substituent on the aromatic ring does not show a great effect on the magnitude of half-wave potential; it is only slightly displaced in the negative direction with respect to (I) when we go from (II) to (III). However, when aromatic substitutents are introduced (IV) a sharp displacement of potential toward positive values takes place.

Though it is as yet too difficult to connect polarographic data with data obtained by other methods, still polarography can play a definite role in elucidating the nature of the given class of compounds.

LITERATURE CITED

[1] J. A. Page, G. Wilkinson, J. Am. Chem. Soc., 74, 6149 (1952); G. Wilkinson, P. L. Pauson, F. A. Cotton, J. Am. Chem. Soc., 76, 1970 (1954); G. Wilkinson, J. M. Birmingham, J. Am. Chem. Soc., 76, 4281 (1954); P. L. Pauson, G. Wilkinson, J. Am. Chem. Soc., 76, 2024 (1954).

[2] C. Furlani, E. O. Fischer, Z. Elektrochem., 61, 481 (1957).

[3] E. O. Fischer, W. Hafner, Z. Naturforsch., 10b, 665 (1955).

[4] A. G. Stromberg, T. A. Markacheva, J. Phys. Chem. 28, 671 (1954).

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DECOMPOSITION OF UNSYMMETRICAL DIARYLIODONIUM SALTS WITH POWDERED BISMUTH IN THE PRESENCE OF BISMUTH TRICHLORIDE

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We have previously [1] discovered that when diaryliodonium chlorides are decomposed with powdered lead in the presence of lead dichloride, organolead compounds are formed in good yields. We have further shown that if unsymmetrical diaryliodonium salts of type ArAr'ICl are decomposed under these conditions, then the more electronegative radical is transferred from the iodine to the lead. Evidently all these reactions proceed through a preliminary stage in which double salts of iodonium and lead chloride are formed; these are then decomposed with lead powder.

In the present paper the results of decomposition of unsymmetrical diaryliodonium salts with powdered bismuth in the presence of bismuth chloride are described. In paper [1] we showed that it is possible to form organo-bismuth compounds by decomposing a double salt of diaryliodonium chloride and bismuth trichloride with powdered elementary bismuth. For experimental reasons, we found it more convenient to use a mixture of Ar_2ICl and $BiCl_3$ instead of a double salt. Under these conditions the yield of triphenylbismuth for example, was 35-40%.

The decomposition of unsymmetrical diaryliodonium salts* was carried out under conditions which gave an optimum yield of triphenylbismuth; a mixture of the iodonium salt and $BiCl_3$ in acetone was decomposed with bismuth powder at room temperature** accompanied by vigorous stirring. After the reaction was completed, the precipitate was filtered out, and the filtrate poured into an ammonia solution. Under this treatment mono and diaryl organobismuth compounds (which presumably are the initial reaction products) change into triaryl compounds. The reactions that take place in this process can be described by the following equations:

$$3\,ArBiCl_2 \rightleftharpoons Ar_3Bi + 2\,BiCl_3$$
$$3\,Ar_2BiCl \rightleftharpoons 2\,Ar_3Bi + BiCl_3$$
$$BiCl_3 + 3NH_4OH \longrightarrow Bi(OH)_3 + 3NH_4Cl$$

* We should note that we obtained unsymmetrical iodonium salts by condensing corresponding iodoso compounds with hydrocarbon under the action of sulfuric acid in an acetic acid medium. We utilized a method described in the literature [2,3] to make iodoso compounds through oxidation of iodine derivatives with peracetic acid. The iodoso compounds that formed were not isolated but condensed directly. In this manner the synthesis of unsymmetrical iodonium salts was accomplished in one stage. The following salts were obtained by this method:

$C_6H_5(p\text{-}CH_3OC_6H_4)ICl$	(76% yield, m.p. 181°),
$C_6H_5(p\text{-}ClC_6H_4)ICl$	(70% yield, m.p. 196°),
$C_6H_5(p\text{-}BrC_6H_4)ICl$	(80% yield, m.p. 193°),
$(p\text{-}CH_3OC_6H_4)\,(p\text{-}C_2H_5OCOC_6H_4)ICl$	(54% yield, m.p. 150°).

** When the reaction was run in boiling acetone or abs. alcohol the yield of organobismuth compound was practically unchanged.

To separate triarylbismuth from inorganic bismuth compound we filtered out the precipitate that formed in ammonia on standing overnight, dried it in air, and extracted with ether. Along with Ar_3Bi the ether took up the aromatic ring-substituted iodine derivative which was formed during decomposition of diaryliodonium salts according to equation

$$3\,(Ar)_2ICl + 2Bi \xrightarrow{(BiCl_3)} Ar_3Bi + 3ArI + BiCl_3$$

The iodine derivative was separated from trialylbismuth by steam distillation.

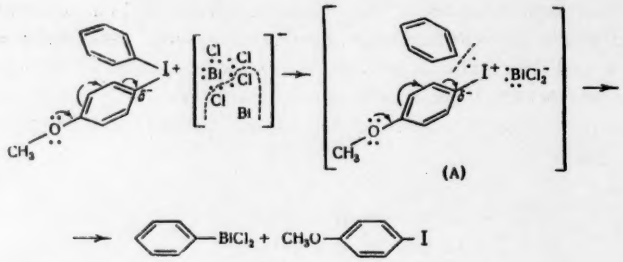
The unsymmetrical diaryliodonium salts that were decomposed as described above, and the products obtained therefrom are listed in Table 1.

TABLE 1

Starting diaryl-iodonium salt	Reaction product	Yield %
$p\text{-}ClC_6H_4)(C_6H_5)ICl$	$(p\text{-}ClC_6H_4)_3Bi$	13
$p\text{-}BrC_6H_4)(C_6H_5)ICl$	$(p\text{-}BrC_6H_4)_3Bi$	16
$p\text{-}CH_3OC_6H_4)(C_6H_5)ICl$	$(C_6H_5)_3Bi$	23
$(p\text{-}CH_3OC_6H_4)(p\text{-}ClC_6H_4)ICl$	$(p\text{-}ClC_6H_4)_3Bi$	19

As it is evident from Table 1, in all the cases the more electronegative radical is transfered to bismuth. In no case were we able to isolate the other product, though it is quite probable that during decomposition of unsymmetrical iodonium salts possessing radicals with small differences in electronegativity a simultaneous transfer of a less electronegative radical to the bismuth is also possible. However, it seems that the second substance is formed in such insignificant amounts that it could only be detected by some physicochemical method, for example chromatographically.

In view of the fact that electron densities are not the determining factors in a radical reaction [4], it would be hard to understand our results if we considered the decomposition of double iodonium salts as homolytic. At the same time, regularities observed by us whereby the more electronegative radical is transferred to the metal could easily be explained by assuming a heterolytic cleavage of double iodonium salts. Then the formation of an organobismuth compound from phenyl-anisyliodonium chloride for example, could be represented as follows:

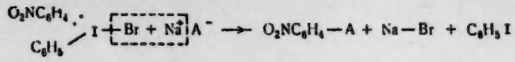


Since the methoxy group acts as an electron donor, a partial negative charge will be induced on the carbon next to the iodine. As a result, the bond between positively charged iodine and anisyl radical becomes stronger.

The phenyl carbon attached to the iodine has a comparatively smaller electron density. Therefore its bond with iodine is not as strong as that of anisyl radical. The splitting out of a phenyl cation and transfer to a negatively charged (in the intermediate complex A) bismuth is more probable than a corresponding splitting of an anisyl cation. This evidently is the reason why organobismuth compounds are formed with more electronegative radicals. The data obtained by Beringer and co-workers [5] provide evidence to support the proposed heterolytic nature of the observed decomposition of iodonium salts. They studied the interactions of unsymmetrical iodonium salts.

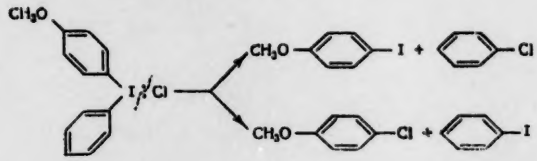
$[(o\text{-}O_2NC_6H_4)C_6H_5IBr$ and $(m\text{-}O_2NC_6H_4)C_6H_5IBr]$ with $NaNO_2$, NaOH, NaCN, CH_3ON_9 etc.

All these reactions (known to be heterolytic) could in general be represented as follows:



Just as in our own case, it was always the more electronegative radical that was transferred to the anion A^-

It is interesting to note that during thermal decomposition of iodonium salts (which proceeds homolytically [6]) a mixture of products is formed, for example:



i.e. the polarity has no observable effect in this case.

Disregarding the fact that there has lately appeared more evidence to support the known role of polar factors in radical reactions, the accumulation of data we presented provides evidence in support of a heterolytic reaction mechanism for the decompositions of double iodonium salts* studied by us.

LITERATURE CITED

[1] O. A. Ptitsyna, O. A. Reutov, M. F. Turchinskii, Proc. Acad. Sci. USSR 114, 110 (1957). **

[2] K. Pausacker, J. Chem. Soc., 1953, 107.

[3] A. Fox, K. Pausacker, J. Chem. Soc,, 1957, 295.

[4] I. Goddard, D. Hey, Quart. Rev., 8, 308 (1954).

[5] F.M.Beringer,U. Drexler, E. Gindler, C. Lumpkin, J. Am. Chem. Soc., 75, 2708 (1953).

[6] R. Sandin, M. Kulka, R. McCready, J. Am. Chem. Soc.,59, 2014 (1937).

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* Two facts could be used as evidence that the reactions in which diaryliodonium chlorides were decomposed with powdered metals proceeded through a double diaryliodonium salt. First is the formation of triphenylbismuth when a double salt of diaryliodonium chloride and bismuth trichloride is decomposed with copper. Also, since copper cannot displace Bi in $BiCl_3$ it would be hard to represent the formation of $(C_6H_5)_3Bi$ in any other way except through a double salt stage.

**Original Russian pagination. See C. B. Translation.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

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